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THE VIBRATION SPECTRA OF CRYSTALS AND THE THEORY OF THEIR SPECIFIC HEATS

By Sir C. V. Raman

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1. Introduction

The thermal energy of a crystalline solid may properly be identified with the energy of vibration of the atoms in it about their positions of equilibrium. The theorem in classical mechanics due to Lagrange[1] which states that a connected system of N particles has 3 N normal modes of vibration enables us to go further and identify the thermal energy with the sum of the energies of these 3 N vibrations, each having its own appropriate frequency. The problem thus reduces itself to that of determining the distribution in frequency of the 3 N vibrations. When this is known, we have only to sum up the expressions for the average energies of the individual vibrations given by Einstein's fundamental theorem[2] to obtain the thermal energy content of the solid at any given temperature.

In the well-known theories of the specific heats of solids due respectively to Debye[3] and to Born and Karman,[4] the frequency distribution is found on the basis of certain special assumptions. Following a suggestion due originally to J. H. Jeans,[5] these authors identify the 3 N vibrations with 3 N different wave-patterns filling the volume of the crystal. The 3 N different frequencies which result from these assumptions make the vibration spectrum of the crystal a diffuse continuum. Lagrange's theorem, however, does not require that a system of N connected particles should necessarily possess 3 N *different* frequencies. Indeed, since a crystal is an assemblage of an immense number of similar groups of particles, we should expect that they would all possess identical frequencies of internal vibration. The recognition of this led the present writer to make a fresh approach to the problem in a paper[6] which was published in these *Proceedings* eight years ago. The results of that paper furnished a simple and forthright explanation of the nature of the vibration spectra of crystals as revealed by the frequency shifts in the scattering of light by them. The theory also indicated some new and previously unsuspected features of these vibration spectra which appeared not inaccessible to observation. Experimental

investigations undertaken to test the predictions of the theory have confirmed their reality. In a recent paper by the writer[7] published in these *Proceedings*, the whole of the work in this field has been reviewed and it has been shown that the behaviour of crystals in light-scattering completely substantiates the correctness of the approach to the subject made in the paper of 1943.

The present paper is a survey of the theoretical aspects of the subject, while the one just referred to dealt with it from the phenomenological standpoint. Its main purpose is to make it clear that the treatment of the theoretical problem given in 1943 was not only on the right lines but was also a complete and rigorous solution of it. The present paper contains also a critical examination of the premises on which the earlier theories of the subject were based. The identification of the normal modes of vibration of the atoms in a crystal with an immense number of wave-patterns comprised in its volume is shown to be an unjustifiable and wholly misconceived hypothesis. It is also shown that the consequences of that hypothesis are contradicted by the facts of observation.

2. Molecular Vibrations in Crystals

We shall commence by considering a simple case which approximates to the actual situation in many crystals and assume that an immense number of molecules, all of the same kind, come together and are held in a regular three-dimensional array by forces which are very weak in comparison with the forces binding the atoms together in each molecule. A substance of this kind would have a low melting point and would sublime very readily. We may cite naphthalene as an example. The molecules of the substance in the state of vapour would move, rotate and vibrate independently of each other. In the crystalline state, their translations could no longer be independent. The free rotations would also be suppressed and replaced by periodic angular oscillations. We shall at first consider here only the internal oscillations of the molecules. In the free state, the modes and frequencies of such internal oscillations would be determined by the geometric form of the molecule, the masses of the atoms comprised in it and the forces holding them together. We may ask ourselves, what would be the situation concerning these vibrations in the crystalline state?

Since by assumption, the intermolecular forces in the crystal are very weak, they could scarcely have any effect on either the modes or the frequencies of molecular vibration. The interactions, however, would have an important consequence, *viz.*, that if any one molecule within the crystal is set

in vibration, its energy would leak away to the other molecules surrounding it, and from these again to other molecules further out, and so forth, so that ultimately the energy would be dissipated through the crystal. The transfer of energy envisaged would be the slower, the weaker the intermolecular forces are, and would take a very long time before it reaches the external boundary of the crystal. It is thus evident that we are here concerned with a diffusion process and not one of wave-propagation. From the assumptions made, it follows that the vibration spectrum of the entire crystal in the frequency region under consideration would differ but little from that of the molecules of which it is composed. In other words, it would exhibit a finite number of monochromatic frequencies.

3. The Effect of Coupling on the Molecular Vibrations

We may now remove the restriction which we laid upon ourselves for the sake of simplicity, *viz.*, that the intermolecular forces were extremely weak. One effect of an increase of their strength would be to speed up the process of diffusion of the energy of vibration from an excited molecule to those surrounding it. Other important effects have also to be considered, *viz.*, an increase in the frequency of the translational-*cum*-rotational oscillations of the molecules about their positions of equilibrium. The coupling between each molecule and its neighbours would also multiply the number of possible modes of their internal vibrations and alter their frequencies.

The problem which here arises was dealt with and solved in the paper of 1943 quoted in the introduction. Every normal mode must satisfy two conditions, *viz.*, that the particles must all vibrate with the same frequency and that their phases must all be the same or opposite. A third condition is set by the nature of the problem in the case of a crystal, *viz.*, that a normal mode should remain a normal mode, following a unit translation of the crystal along any one of the three axes of the lattice. These three conditions taken together completely determine the possible modes of vibration of the structure of the crystal. There are only two possibilities in respect of the phases of vibration in successive cells of the structure along each axis, *viz.*, that they are the same or else alternate. Thus, in all, there are $2 \times 2 \times 2$ alternative possiblities and therefore eight species of normal modes. The $3p$ equations of motion of the p atoms in the unit cell of the structure would necessarily be different in each species. Thus we have $8 \times 3p$ or $24p$ equations of motion and the same number of solutions. Only $(24p-3)$ solutions would represent actual vibrations, while the 3 excluded solutions would represent simple translations.

Thus, when the finiteness of the intermolecular forces is taken into account, the structure of the crystal has $(24p-3)$ modes of vibration, each with its appropriate monochromatic frequency. These would include the translational-*cum*-rotational oscillations of the molecules which are possible by reason of their being held in a regular three-dimensional array. If we imagine the strength of the intermolecular forces to be gradually reduced, the frequency of such oscillations would diminish steadily, while the frequencies of the vibrational modes which are multiplied 8-fold in number by the coupling would converge towards the vibrational frequencies of the molecules in the free state.

4. The Enumeration of Wave-Patterns

We turn now to the examination of the premises on which the specific heat theories of Debye and Born-Karman are based. The enumeration according to frequency or wave-length of the stationary wave-patterns within an enclosure is effected, following Rayleigh,[8] by assuming for the latter a cubical shape, and counting up the terms of a three-dimensional Fourier expansion which individually are solutions of the wave-equation valid inside the enclosure. It is essential for the argument that the waves travel freely within the enclosed space and are not subject to damping. The slightest damping of the waves during their progression would invalidate the entire procedure. We have, in fact, only to assume that the enclosure is large enough; the waves, if damped, would die away before they could traverse it from end to end and return to build up a stationary interference pattern. On the other hand, wave-propagation in material media is necessarily damped to an extent determined by the physical state of the medium and the wave-length or frequency of the vibration. Indeed, it may well happen that such damping is so enormous as altogether to preclude the possibility of wave-propagation through the medium. Hence, it follows that the identification of the normal modes of atomic vibration within material bodies with stationary wave-patterns determined by the external boundary conditions is a wholly misconceived and erroneous hypothesis.

We may illustrate the foregoing remarks by two typical examples. In the paper already cited, and again later in his book,[9] J. H. Jeans put forward a mathematical argument based on the Fourier analysis which claims to prove that the energy of the translatory motion of the molecules in a gas can be identified with the energy of an appropriately chosen number of sound-wave trains in it, the great majority of them having wave-lengths of the same order of magnitude as the mean distance between neighbouring molecules. The proof is, however, illusory, since it overlooks the fact that

sound-waves in gases are damped by viscosity. No wave-propagation is possible in a gas if the wave-length is as small as the molecular mean free path, and this is itself many times larger than the average distance between neighbouring molecules. In other words, the sound-waves proposed to be enumerated by Jeans have no physical existence !

The second example which we shall consider is that already dealt with in Section 2 above. It is evident that a crystal consisting of discrete molecules having their own characteristic frequencies of vibration would present an impenetrable obstacle to the entry and propagation through the substance of " waves " having those self-same frequencies. We have only to recall in this connection the optical behaviour of a cell containing the vapour of sodium or of mercury towards the entry into it of the resonance radiations from a sodium vapour or a mercury vapour lamp respectively, or the behaviour of a rock-salt crystal towards the entry into it of infra-red radiations previously monochromatised by successive reflections at the surfaces of crystals of the same substance. Since the waves cannot even enter the medium, it would be clearly be a fantastic procedure to identify the molecular vibrations with wave-patterns enumerated on the basis of their free propagation inside the crystal.

5. Wave Propagation in Periodic Structures

The title of this section is the same as that of a book[10] by L. Brillouin which was published a few years ago, having the sub-title " Electric Filters and Crystal Lattices". The greater part of that book is devoted to an exposition of the ideas underlying the Debye and Born-Karman theories of crystal behaviour, and it is therefore appropriate that some reference is made to it here. Surprisingly enough, though the book concerns itself with the problem of finding the frequency spectra of crystals, one searches its pages in vain for any reference to the normal modes of vibration of the atoms in a crystal. It would seem, in fact, that Brillouin considers " waves " and " normal modes " as equivalent expressions. This is clearly a misconception. While the fundamental theorem of Lagrange enables us to enumerate the normal modes of vibration of a system, a " wave " is not a normal mode since the phase of the motion in it changes from point to point and from instant and instant, and hence one cannot, in general, enumerate waves. Only when there is perfectly undamped wave-propagation within a perfectly reflecting enclosure does the restriction of the permitted wave-lengths to a specifiable but infinite sequence of values resulting therefrom enable us to regard the stationary wave-patterns as equivalent to normal modes. But as already pointed out in the preceding section, there can be no undamped

wave-propagation in any material substance consisting of atoms and molecules. It follows that the contents of Brillouin's book are without significance in relation to the problems of crystal physics which it professes to deal with.

The behaviour of macroscopic systems exhibiting some sort of periodicity in their structure, *e.g.*, a stretched string loaded at regular intervals with masses of the same or different kinds, is the theme with which most expositions of the Born-Karman theory commence. It is, therefore, necessary to examine the question whether the behaviour of crystals can at all be compared with those of mechanical models, and if so, with what limitations.

Three basic facts about crystals which we can never hope to reproduce in any artificially constructed mechanical model are, *firstly*, the immense numbers of individual particles constituting even the smallest of crystals: *secondly*, the possibility of independent movement of the atoms and molecules which reveals itself in various ways, and *thirdly*, the high frequencies of vibration which lie mostly far above the limits of validity of the classical mechanics. Besides these vital differences, it should also be pointed out that no macroscopic model can claim to represent the behaviour of a crystal unless it satisfies the conditions requisite for dynamic similarity. In other words, the linear dimensions, masses and operative forces in the model should be so proportioned to those of the crystal that the actions taking place in the latter are reproduced in the former. If such a model were constructed—even if it be only on paper—it would immediately make it evident that its behaviour, far from supporting the Born lattice dynamics, would show its basic assumptions to be untenable.

6. Mechanical Models of Crystal Behaviour

We shall illustrate the foregoing remarks by considering a model of a diamond crystal, enlarged in its linear dimensions by a factor of 10^7 so that the individual atoms can be conveniently observed, and slowed down in the time-rate of its actions by a factor of 10^{12} so that the movements of the atoms can be visually followed. In the actual crystal, assumed to be 1·54 millimetre in diameter, the highest characteristic frequency of atomic vibration is 1332 cm.$^{-1}$ in spectroscopic units, while the highest sound velocity is 18,000 metres per second. In the model which is 15·4 kilometres in diameter, the characteristic frequency is slowed down to 40 vibrations per second, while the fastest sound wave would take 24 hours to travel from the centre of the model to its surface and return again after reflection to the centre. Let us now suppose that a group of atoms near the centre of the model is set in motion by impulses so directed that all of them move

together initially in the same direction and with the same velocity. It is evident that this would result in an elastic wave which would spread outwards from the centre towards the surface of the model and return again to the centre after travelling 15·4 kilometres in 24 hours, provided, of course, that in the course of this lengthy excursion, its energy has not dissipated itself completely. Then again, let us suppose that in another experiment, the same group of atoms is excited by two simultaneous sets of impulses so directed that the atoms belonging to the two interpenetrating Bravais lattices commence moving with equal velocities in opposite directions. In this case, it is easily seen that the result of the impulses would be to set up, not a travelling wave, but a local oscillation of the two lattices with respect to each other which would gradually spread outwards. Observations during a brief period of 60 seconds would suffice for a count of 2400 complete periods of the oscillation and hence also for a precise determination of its frequency. The presence of an external boundary many kilometers away from the centre of disturbance could obviously have no influence whatever on the phenomena taking place during those 60 seconds. In other words, the nature and frequency of the oscillation excited by the impulses would depend solely on the structure of the model and on no other considerations.

We may summarise the lessons taught by our model in the following two statements. (I) *The elastic vibrations in a crystal are a consequence of the translatory movements of its volume elements and therefore also of its lattice cells; they extend through the volume of the crystal, and their frequencies are low and form a diffuse continuous spectrum.* (II) *The characteristic vibrations in a crystal represent the internal oscillations of the units of its structure; they are highly localised and their frequencies are also high and have sharply defined values constituting a line-spectrum.*

7. Born's Lattice Dynamics and Its Consequences

Whereas Debye restricted himself for the most part in his original paper to " monoatomic " solids, in other words to crystals having relatively simple structures, no such restriction is contemplated in the Born-Karman theory. Indeed, the claim made on behalf of the latter is that it specifically takes into account the lattice structure of the crystal and embraces in its scope the case of complex structures containing many atoms per unit cell. If there be p atoms in each cell, and N cells in the crystal, the total of 3 Np degrees of atomic freedom of movement are identified with the same number of wave-patterns in the crystal. 3 N wave-patterns represent the " acoustic " branches of the spectrum, and the remaining $(3p-3)$ N wave-patterns the " optical " branches. Each wave-pattern is identified with one of the terms in a three-

dimensional Fourier expansion, and the summation of all the terms with the totality of the possible vibrations in the crystal.

As has already been shown earlier in the paper, the identification of normal modes with wave-patterns is theoretically not a permissible procedure in the case of material media, and hence the entire structure of the Born lattice dynamics falls to the ground. It is unnecessary in these circumstances for us to consider the question dealt with in a paper by Ledermann[11] whether the so-called "cyclic postulate" is or is not an appropriate way of getting over the difficulty of the unknown boundary conditions at the external surface of a crystal. On the other hand, it might be useful to consider what the actual consequences of the Born lattice dynamics are in relation to the nature of the vibration spectra of crystals, so that we could proceed to compare them with the facts of experiment.

It is an immediate consequence of the Born-Karman theory that the vibration spectrum of a crystal presents the aspect of a diffuse continuum throughout the entire range of frequency. This is apparent from the numerous diagrams printed in Brillouin's book and from the calculations for various cases published by Born and his collaborators. The reason for it is also obvious. Since the wave-patterns form a Fourier sequence, their wave-lengths are crowded together as we approach the limit where the sequence is assumed to be terminated and the wave-lengths are therefore of the same order of magnitude as the lattice spacings of the crystal. A difference in wave-length necessarily means a change in frequency, and the variations thus arising become large for the "optical branches" of the spectrum near the lower limit of wave-length. Hence the frequency spectrum is spread out very widely in this region. But the spread is far from being negligible even in the range of greater wave-lengths. Though no actual calculations have been published for the case of crystals containing ions or molecules having their own characteristic frequencies of vibration, one may feel sure that if such calculations were made, the result would not exhibit any visible resemblance to the vibration spectra of such ions or molecules as we actually know them from experimental studies.

8. The Scattering of Light in Crystals

For reasons which can well be understood, a crystal is intensely opaque to electromagnetic radiations over a wide range of frequency on either side of its own characteristic frequencies in the infra-red. In consequence, only rather vague and fragmentary indications were available regarding the nature of the vibration spectra of crystals, until the spectroscopic study of the scattering of light introduced a new and simple as well as powerful and

accurate way of exploring this field of knowledge. From the analogies presented by the case of gases, liquids and amorphous solids where the same method is equally applicable, it is obvious that the frequency shifts observed in light scattering furnish us with a straight answer to the question of the nature of the vibration spectrum of a crystal, *viz.*, that it consists of a set of sharply-defined monochromatic frequencies in the infra-red. The general acceptance of this simple view of the case has, however, been held up by the belief in theories which were put forward at a time when there was no experimental knowledge which could set theoretical thinking on the right path. To get over the patent contradiction between those theories and the experimental facts, it was suggested that while the real vibration-spectrum is continuous, the frequency shifts observed in light-scattering represent the result of the elimination of everything except the so-called limiting frequencies of vibration with large wave-lengths by a selection principle based on the idea that the mechanical waves give a coherent reflection of the incident light waves, while the rest of the spectrum is hidden away from sight by a species of optical interference.

That the way proposed for escape from the difficulties is not a reasonable one becomes evident when it is recalled that large frequency shifts are also observed in the scattering of light by the molecules of gases and of liquids. They are very properly described in these cases as the result of an incoherent scattering in which the individual molecules of the substance exchange energy with the incident radiation. If this be a correct description of the process in the cases of fluid media, there is no reason why the obviously analogous effects observed with crystals should be regarded differently and ascribed to a coherent reflection of the light waves by mechanical waves. The mere change from a fluid to the solid state cannot be claimed as a justification, for it is found that organic glasses also give sharply-defined lines as frequency shifts in light-scattering. Such glasses are solids in every sense of the term, and since they do not possess any periodicity of structure, it is not possible in their case to invoke any selection principle which could convert a diffuse continuum into a line spectrum.

Another observed fact which is absolutely fatal to the Born lattice dynamics is the appearance in numerous cases of sharply-defined lines as frequency shifts which do not agree with the fundamental frequencies of vibration, but are overtones or summations thereof. For frequency shifts of this kind to appear, it is essential that the amplitude of the atomic oscillations should be comparable with the interatomic distances, and this again would not be possible if the energy-quantum of the particular frequency

is distributed as a wave extending over the whole volume of the crystal or even any limited region inside it. Overtones and summations could appear as frequency shifts with the observed intensities only if the oscillations are highly localised, in other words, are restricted to volumes which are comparable in their dimensions to the unit cells of the crystal structure. It is clearly not possible in these circumstances for the proposed selection principle to function which would pick up a single frequency from a continuous spectrum of frequencies.

Finally, we may refer to the specially interesting cases, of which diamond is the best example, in which strongly exposed spectrograms reveal frequency shifts appearing as sharply-defined lines which are not explicable as overtones or summations of the $(3p-3)$ normal modes in which the phase is the same in adjacent lattice cells of the crystal lattice, but which compel the 21 p additional modes in which the phase alternates also to be considered. Diamond, for instance, exhibits besides the line with a frequency shift of 2664 cm.$^{-1}$ which is the octave of the principal frequency of 1332 cm.$^{-1}$, also several other lines as frequency shifts which are identifiable as overtones and summations of the eight fundamental frequencies of the diamond structure. In a recent paper in these *Proceedings*, P. S. Narayanan[12] has described and discussed the results of his studies on the case of diamond and shown that they are altogether incompatible with the consequences of the Born lattice dynamics. It is unnecessary to re-traverse the same ground here.

Summary

The enumeration of wave-patterns within an enclosure on a scale of wave-lengths or frequencies presupposes that the waves are perfectly undamped and that the enclosure is perfectly reflecting. In any material medium, however, wave-propagation is necessarily damped and such damping may be so enormous as altogether to preclude wave-propagation. It follows that it is not permissible to identify the modes of atomic vibration in crystals with wave-patterns. Since the specific heat theories of Debye and of Born-Karman are based on such identification, they cannot be sustained.

For any mechanical model to represent the dynamic behaviour of a crystal, it is necessary that it should satisfy the requirements for dynamic similarity. When these requirements are satisfied, the behaviour of the model does not support the ideas underlying the Debye and Born-Karman theories, but on the other hand agrees with the results of the theory of the dynamics of crystal lattices put forward by the writer in 1943.

The phenomena of light-scattering observed in crystals are also discussed and it is shown that the experimental facts are incompatible with the ideas underlying the Born-Karman theory.

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INTERACTION OF HYDROXY ACETOPHENONES AND THEIR DERIVATIVES AND THIONYL CHLORIDE IN PRESENCE OF FINELY DIVIDED COPPER

Part IV. Preparation of 3 : 3′-Diacetyl-4 : 4′-dihydroxy-6 : 6′-dibenzyloxy-diphenyl thioether and its derivatives

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2-Hydroxy-4-benzyloxy-acetophenone, thionyl chloride and chloroform were mixed together and copper powder was gradually added to it when the thioether was obtained. This thioether gave 2-hydroxy-4-benzyloxy-5-bromo-acetophenone[1] when treated with bromine in acetic acid medium and when treated with concentrated nitric acid in acetic acid medium, it gave a mono nitro compound which on debenzylation with hydrobromic acid gave 2 : 4-dihydroxy-5-nitro-acetophenone.[2] This proved that the thioether was 3 : 3′-acetyl-4 : 4′-dihydroxy-6 : 6′-dibenzyloxy-diphenyl thioether.

Methylation, acetylation and benzoylation gave dimethoxy, diacetoxy and dibenzoyloxy derivatives of the thioether. Phenyl-hydrazine gave diphenyl hydrazone of the thioether.

The same ketone gave the same thioether with (i) sulphur mono-chloride and (ii) sulphur dichloride in presence of traces of copper and hence the mechanism of the reaction can be explained in the same way as is done by Hirve, Jadhav and Chakradeo.[3]

Experimental

3 : 3′-Diacetyl-4 : 4′-dihydroxy-6 : 6′-dibenzyloxy-diphenyl thioether (*I*)

2-Hydroxy-4-benzyloxy-acetophenone (12 g.) and thionyl chloride (20 g.) were mixed together and dry chloroform (20 c.c.) was then added to the mixture. It was surrounded by crushed ice when copper powder (8 g.) was gradually added to it. The reaction mixture was left overnight at room temperature and next day more dry chloroform (20 c.c.) was added and it was heated on a water-bath at 60° for about ten minutes. The solution was filtered and the residue was again extracted with chloroform. A pasty greyish

residue was obtained after the removal of the liquid. Pinkish white solid was obtained after repeatedly washing the mass with acetone. It finally crystallised from acetic acid in white needles, m.p. 202–3°. It gave greenish coloration with alcoholic ferric chloride solution. It was soluble in benzene, carbon tetrachloride, carbon disulphide and alcohol and insoluble in ether and petrol. Found: S, 6·4; $C_{30}H_{26}O_6S$ requires S, 6·2 per cent. This same substance was obtained by the interaction of the ketone (2 g.), sulphur monochloride (1 g.) or sulphur dichloride (1 g.) and copper powder (a few milligrams) in presence of dry chloroform and the reaction was carried out and finished as above. The compound showed no lowering in melting point with the above thioether.

Phenylhydrazone of 3: 3′-*diacetyl*-4: 4′-*dihydroxy*-6: 6′-*dibenzyloxy-diphenyl-thioether*

It was prepared by heating acetic acid solutions of the reactants on a boiling water-bath for half an hour. The product separated on cooling. It crystallised from acetic acid, m.p. 239–40°. Found: N, 8·2; $C_{42}H_{38}O_4N_4S$ requires N, 8·1 per cent.

3: 3′-*Diacetyl*-4: 4′-*dimethoxy*-6: 6-*dibenzyloxy-diphenyl thioether*

Methylation was carried out by dimethyl sulphate in presence of acetone as usual by heating the mixture on a boiling water-bath for about an hour. It crystallised from alcohol in brown plates, m.p. 128–29°. Found: S, 5·8; $C_{32}H_{30}O_6$ S requires S, 5·9 per cent.

3: 3′-*Diacetyl*-4: 4′-*dibenzoyloxy*-6: 6′-*dibenzyloxy-diphenyl thioether*

Benzoylation was carried out by heating the reactants in presence of a few drops of pyridine for ten minutes at 170–80°. On mixing the reaction mixture with crushed ice a brown liquid separated. It was extracted with ether and the pasty solid left after the removal of ether was triturated with dilute caustic soda solution and finally crystallised from alcohol, m.p. 107–9°. Found: S, 4·6; $C_{44}H_{34}O_8$ S requires S, 4·4 per cent.

3: 3′-*Diacetyl*-4: 4′-*diacetoxy*-6: 6′-*dibenzyloxy-diphenyl thioether*

Acetylation was carried out as usual by boiling the substance with acetic anhydride in pyridine solution for three hours. The pasty mass obtained on dilution was repeatedly washed with dilute hydrochloric acid and finally crystallised from acetic acid as dark brown crystals, m.p. 173–75°. Found: S, 5·4; $C_{34}H_{30}O_8$ S requires S, 5·3 per cent.

2-Hydroxy-4-benzyloxy-5-bromo-acetophenone

The thioether (I) (1 g.) was dissolved in boiling acetic acid (10 c.c.). When the solution cooled to 90°, a crystal of iodine was added and 15 per cent. solution of bromine in acetic acid (5 c.c.) was added and the reaction mixture was shaken for eight hours and then left overnight at room temperature. Acetic acid was allowed to evaporate at room temperature. Solid began to separate after one day which was finally crystallised from alcohol and ethylacetate mixture in white needles, m.p. 154–55°. Found: Br, 24·7; $C_{15}H_{13}O_3Br$ requires Br, 24·9 per cent.

2-Hydroxy-4-benzyloxy-5-nitro-acetophenone

The thioether (I) (0·5 g.) was suspended in acetic acid (5 c.c.) and concentrated nitric acid (5 c.c.) was slowly added to it and the mixture left overnight at room temperature. Next day crystals had separated which were filtered and recrystallised from alcohol in white needles, m.p. 140–41°. Found: N, 5·3; $C_{15}H_{13}O_5N$ requires N, 4·9 per cent. When boiled with hydrobromic acid in presence of acetic acid this benzyloxy compound gave 2:4-dihydroxy-5-nitro-acetophenone.

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ANALYSIS OF THE RAMAN SPECTRA OF SODIUM AND POTASSIUM TARTRATES

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1. Introduction

In a previous communication to these *Proceedings*, the author (Padmanabhan, 1948) reported some preliminary investigations on the Raman spectra of crystalline potassium and sodium tartrates. These studies have now been extended. The intensity and state of polarisation of the intense Raman lines in the spectra of both sodium and potassium tartrates have been estimated for different orientations of the crystal relative to the directions of incidence and observation, incident light being unpolarised. The results are presented below.

2. Experimental Details

The crystals were cut in the form of a rectangular parallelopiped ($2 \times 1 \cdot 5 \times 1$ cm.), with its edges along the axis α, β and γ where, α, β and γ represent the directions of minimum, medium and maximum refractive indices respectively. A sealed horizontal mercury arc which was water cooled and magnet controlled served as a source of intense λ 2537 radiation. The arc was covered except for a rectangular aperture ($1 \cdot 5 \times 0 \cdot 5$ cm.) which was used to limit the beam. The light emerging through it was condensed by a quartz lens of focal length 4 cm. in the ultra-violet region and was allowed to be incident on the required face of the crystal. The light scattered by the crystal was condensed on to the slit of a Hilger Intermediate quartz spectrograph by a quartz lens of focal length 9 cm. in the ultra-violet. In order to study the polarisation characteristics of the scattered light a double-image prism with its principal planes horizontal and vertical was interposed in the path of the scattered beam between the crystal and the condensing lens. Six different spectrograms were obtained by varying the orientation of the crystal with respect to the directions of illumination and observation and the scattered beam was analysed in each case. With a slit width of 0·1 mm. and using Ilford Special Rapid plates, exposures of the order of 3 days were given in each case to record the spectrum with reasonable inten-

sity. The polarisation characteristics of the feebler Raman lines could not be studied, since exposures long enough to record them would have obliterated the polarisation data of the more intense lines due to over-exposure. The different spectra were obtained under similar conditions of duration of exposures, optical arrangement, etc. Due to the long exposures that had to be given and consequent changes in the intensity of emission of the arc, great accuracy is not claimed for the values given below for the relative intensities of the same Raman lines appearing in different spectrograms. An arbitrary value of 20 is assigned to the intensity of the strongest line in each plate and the intensities of all other lines are expressed in relation to this figure.

3. Results and Discussion

Sodium tartrate ($Na_2C_4H_4O_6$, $2H_2O$) crystallises in the orthorhombic class (space group V^2) and has four molecules in a unit cell. Potassium tartrate ($K_2C_4H_4O_6$, $\frac{1}{2}H_2O$) belongs to monoclinic class. Its crystal structure has not been analysed so far.

In the case of orthorhombic crystals, there exist four types of oscillations, *viz.*, symmetric (A_1) and antisymmetric (B_1, B_2 and B_3). The polarisability tensor corresponding to these four types of oscillations are given as (Mathieu, 1945)

$$A_1 \quad \begin{vmatrix} \epsilon_{xx} & 0 & 0 \\ 0 & \epsilon_{yy} & 0 \\ 0 & 0 & \epsilon_{zz} \end{vmatrix} \qquad B_1 \quad \begin{vmatrix} 0 & 0 & 0 \\ 0 & 0 & \epsilon_{yz} \\ 0 & \epsilon_{zy} & 0 \end{vmatrix} \qquad B_2 \quad \begin{vmatrix} 0 & 0 & \epsilon_{zx} \\ 0 & 0 & 0 \\ 0 & \epsilon_{xz} & 0 \end{vmatrix} \qquad B_3 \quad \begin{vmatrix} 0 & \epsilon_{xy} & 0 \\ \epsilon_{xy} & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix}$$

Let O X Y Z be the fixed co-ordinate system in space and let the incident light be along OX and scattered light along OY. In biaxial crystals there are six possible states of arrangement of the crystal *oxyz* (where *ox*, *oy*, *oz* are the crystallographic axes which coincide with α, β and γ respectively in the case of orthorhombic crystals) with respect to the fixed co-ordinate axes as shown below.

X Y Z	X Y Z	X Y Z	X Y Z	X Y Z	X Y Z
x y z	*y x z*	*x z y*	*z x y*	*y z x*	*z y x*
1	2	3	4	5	6

The vaues of the depolarisation factor in all these different cases for different types can be easily written down as follows:

TABLE I

Polarisation Values

Type \ Case	1	2	3	4	5	6
A_1 ..	0	0	0	0	0	0
B_1 ..	0	~	0	~	~	~
B_2 ..	~	0	~	~	0	~
B_3 ..	~	~	0	0	~	0

It can be seen from above, that three cases of study are enough to analyse the spectrum completely. In the case of sodium tartrate only five cases were studied and the approximate depolarisation values of the different Raman lines are entered in Table II. In Fig. 1 is reproduced a typical spectrogram corresponding to the setting 6.

TABLE II

Polarisation Data for Sodium Tartrate

Frequency	Case 1	Case 2	Case 4	Case 5	Case 6	Type
42	0	0	0	0	0	A_1
83	..	0	0	0	0	A_1
110	~	~	0	0	·5	B_3
134	~	~	0	0	·5	B_3
188	~	0	~	0	~	B_2
234	0	~	~	..	*f*	B_1
279	..	~	0	..	*f*	B_3
353	..	~	0	..	0	B_3
532	0	~	..	0	~	A_1+B_2
811	0	~	~	~	~	B_1
893	~	~	·5	~	·5	B_3
990	0	·5	·5	..	=1	A_1
1112	~	~	0	~	0	B_3
1210	~	~	0	~	0	B_3
1352	~	~	0	..	..	B_3
1380	~	~	..	~	0	B_2+B_3
1404	·5	0	0	..	·5	A_1
1432	~	~	~	~	~	B_2+B_3
1560	~	~	·5	~	·5	B_3
1585	~	~	0	~	·5	B_3
2935	~	0	..	0	~	B_2
2981	0	~	0	~	~	B_1
3285	0	~	~	~	~	B_1
3399	0	~	~	~	~	B_1
3471	0	·5	0	0	0	A_1

(*f* = faint)

In a monoclinic crystal, there arise only two types of oscillations symmetric (S) and antisymmetric (A) with respect to the binary axis (which coincide with β). The corresponding tensor components are

$$(S)\begin{vmatrix} \epsilon_{xx} & 0 & \epsilon_{xz} \\ 0 & \epsilon_{yy} & 0 \\ \epsilon_{zx} & 0 & \epsilon_{zz} \end{vmatrix} \quad \text{and (A)} \quad \begin{vmatrix} 0 & \epsilon_{xy} & 0 \\ \epsilon_{yx} & o & \epsilon_{yz} \\ 0 & \epsilon_{zy} & 0 \end{vmatrix}$$

Table III gives the different possible orientations of the crystal and the corresponding surviving tensors in the horizontal and vertical components of the scattered beam (Rousset, 1947).

TABLE III

Case	Orientation of the crystal	Horizontal Component	Vertical Component
1	OX$-o\gamma$; OY$-o\alpha$; OZ$-o\beta$	$\epsilon_{yz}^2+\epsilon_{yx}^2$	$\epsilon_{zz}^2+\epsilon_{zx}^2$
2	OX$-o\gamma$; OY$-o\beta$; OZ$-o\alpha$	$\epsilon_{yx}^2+\epsilon_{yz}^2$	$\epsilon_{xx}^2+\epsilon_{zx}^2$
3	OX$-o\alpha$; OY$-o\gamma$; OZ$-o\beta$	$\epsilon_{xz}^2+\epsilon_{xy}^2$	$\epsilon_{zz}^2+\epsilon_{zy}^2$
4	OX$-o\beta$; OY$-o\gamma$; OZ$-o\alpha$	$\epsilon_{xz}^2+\epsilon_{zy}^2$	$\epsilon_{xx}^2+\epsilon_{xy}^2$
5	OX$-o\beta$; OY$-o\alpha$; OZ$-o\gamma$	$\epsilon_{zy}^2+\epsilon_{zx}^2$	$\epsilon_{yy}^2+\epsilon_{yx}^2$
6	OX$-o\alpha$; OY$-o\beta$; OZ$-o\gamma$	$\epsilon_{xy}^2+\epsilon_{xz}^2$	$\epsilon_{yy}^2+\epsilon_{yz}^2$

(β, the binary axis coincides with $o\gamma$).

As can be seen from the above table, cases 1 and 2 are alone sufficient to find out the symmetric and antisymmetric types of oscillations. Further, in the two cases, while the horizontal component containing the anti-symmetric tensor remains unchanged the vertical component containing the symmetric lines changes from $(\epsilon_{zz}^2+\epsilon_{zx}^2)$ to $(\epsilon_{xx}^2+\epsilon_{zx}^2)$. In the other cases, the horizontal and vertical components contain both the symmetric, as well as anti-symmetric lines.

Table IV gives the intensities of the various Raman lines in different cases in the horizontal and vertical components. The Raman spectrum with the scattered beam analysed (Case 1) is reproduced in Fig. 2.

External Vibrations.—Of the five low frequency oscillations 42, 83, 110, 134 and 188 recorded in sodium tartrate, 42 and 83 are symmetric while the rest are antisymmetric. The two lines at 110 and 134 which are found to be very intense in case 2 may be assigned as due to rotatory type of oscillations of the tartrate ion around the axis OY. The fact that they do not

TABLE IV

INTENSITIES

Type	Frequency	Case 1		Case 2		Case 3		Case 4		Case 5		Case 6	
		Hor.	Ver.	Hor.	Ver.	Hor.	Ver	Hor.	Ver,	Hor.	Ver.	Hor.	Ver.
S ..	33	..	5	..	8	8	3	3	8	2	6	2	2
A ..	76	18	..	10	..	18	3	2	5	10	2	6	2
S ..	108	..	8	..	15	6	12	8	15	..	8	..	3
A ..	153	3	..	3	..	2	2	2	..	5	1	5	1
S ..	172	..	6	..	12	12	6	7	12	..	8	5	1
A ..	281	2	..	2	..	2	1	..	2	4	1	3	1
A ..	339	1	..	2	..	..	..	..	..	2	.	2	1
A ..	379	1	..	3	..	..	..	3	1	5	2	3	1
A ..	493	..	..	1	..	2	..	1	3	2	..	1	1
A ..	532	1	..	8	..	3	1	7	5	4	..	3	1
A ..	805	10	2	15	2	10	10	15	7	6	3	6	2
S ..	850	..	2	..	2	2	2	..	3	5	2	5	2
A ..	897	10	..	1	1	12	3	3	5	6	2	3	..
A ..	917	3	..	..	..	6	..	3	6	..	2	..	..
A ..	990	2	..	8	3	..	..	15	10	..	..	..	..
A ..	1072	2	..	2	..	6	..	..	3	6	1	2	..
A ..	1110	8	..	8	..	8	10	8	3	6	4	1	..
S ..	1218	..	3	..	6	3	6	4	2	10	2	..	..
A ..	1244	5	..	3	..	6	6	..	3	..	2	3	..
A ..	1289	..	..	2	..	..	..	..	..	..	3	..	..
A ..	1322	6	3	..	8	6	5	6	8	15	8	15	4
A+S ..	1397	20	10	8	12	15	2	2	15	20	8	20	3
S+A ..	1428	20	10	8	12	20	10	10	15	..	6	20	3
A+S ..	1585	5	3	5	3	3	6	8	4	4	..	..	2
A+S ..	1628	3	3	8	3	3	6	8	3	..	..	..	..
A+S ..	2926	20	8	20	15	20	12	20	20	20	12	20	6
A ..	3283	15	2	12	2	10	5	15	10	..	5	5	..
S ..	3376	2	5	..	7	..	3	5	2	8	..	5	1
A ..	3435	5	2	8	3	5	3	5	1	2	1	2	..

appear in case 4 confirms this assignment. The two frequencies 42 and 83 may be due to translatory type of oscillations.

In the case of potassium tartrate, Table III and Fig. 2 show that the lines 76 and 153 do not appear in the vertical component of the scattered beam. These two can therefore be taken as antisymmetric lines. The rest 33, 108 and 172 are symmetric lines. The values of their intensities suggest that out of these five lines, 76, 108 and 172 are due to rotatory type of oscillations and 33 and 153 as due to translatory type of movements. The line at 172 appears with considerable intensity in the horizontal component of case 3 and vertical component of case 4 and hence it can be regarded as due to the rotatory type of oscillations of the tartrate ion round the binary axis.

Internal Vibrations.—The two lines at 2981 and 2935 in sodium tartrate, due to C—H oscillations are attributed to B_1 and B_2 type of oscillations. The behaviour of the corresponding line 2976 cm.$^{-1}$ in potassium tartrate is not strictly characteristic of the symmetric or antisymmetric type of motions and so it is assigned as due to the combination of the two. Four other lines 1628, 1585, 1428 and 1397 cm.$^{-1}$ are also found to be combination of the two types. The line at 990 cm.$^{-1}$ in sodium tartrate is symmetric while the corresponding line in potassium tartrate is antisymmetric. As the crystal structures are not fully known, it is difficult to discuss the nature of the oscillations.

Of the three water bands that are analysed in sodium tartrate, the bands at $\sim$3471 and 3399 exhibit polarisation values corresponding to antisymmetric and symmetric types. It is interesting to note that this observation is in accordance with the findings of Chapelle (1948) in Rochelle salt, while in the case of potassium tartrate, the band $\sim$3376 is found to be symmetric and the band $\sim$3435 antisymmetric.

I thank Professor R. S. Krishnan for his inspiring guidance.

Summary

The polarisation characteristics of the light scattered by single crystals of sodium and potassium tartrates have been investigated using the mercury resonance radiation as exciter. The study revealed that the behaviour of the Raman lines in sodium tartrate and potassium tartrate satisfied the selection rules for the orthorhombic and monoclinic symmetry respectively.

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Fig. 1

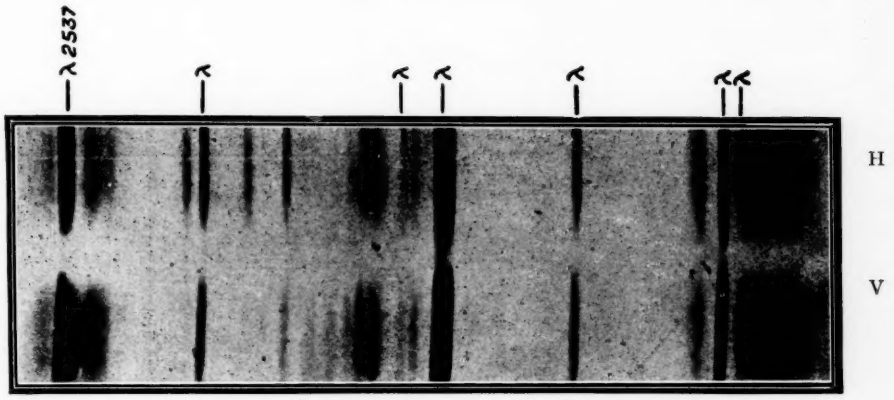

Fig. 2

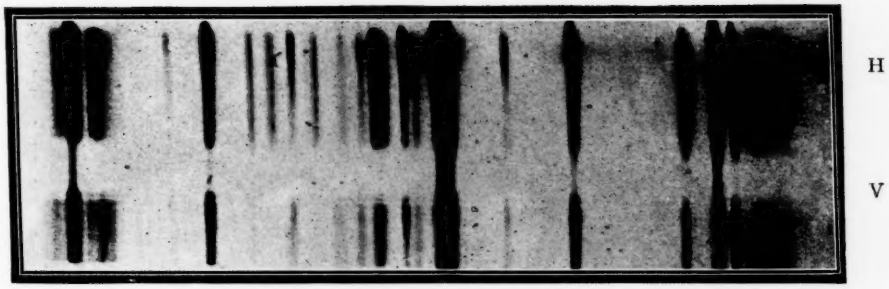

FIG. 1. Raman spectrum of Sodium tartrate—Case 6

FIG. 2. Raman spectrum of Potassium tartrate—Case 1

PHOTOELASTIC PROPERTIES OF BARITE

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1. Introduction

Even though the phenomenological theory of photoelasticity was developed for all the crystal classes as early as 1889 by Pockels, so far measurements on the photoelastic constants were mostly confined to crystals belonging to the trigonal system and to those possessing still higher symmetry. In fact, the only crystal amongst the optically biaxial group, whose photoelastic behaviour has been thoroughly investigated is topaz (Eppendahl, 1920), belonging to the rhombic holohedral class. Recently the photoelastic properties of some of the important crystals belonging to the cubic system have been investigated by Ramachandran (1947, 50), Bhagavantam and Suryanarayana (1947, 1949), and Burstein and Smith (1948). The author has determined the photoelastic constants of barite which belongs to the same crystal class as topaz, and the results are reported in this paper.

A knowledge of the photoelastic properties of barite is of great interest in view of the fact that its elastic constants are very small compared to those of topaz. Hence it is natural to expect that such a wide difference between the elastic constants of these two minerals should manifest itself prominently in their photoelastic behaviour as well. This is actually found to be the case. The variation of the optical properties of barite under hydrostatic pressure has also been investigated. The true temperature coefficients of the three principal refractive indices of barite have been calculated from the already known data on its thermo-optic behaviour (Radhakrishnan, 1951) and its thermal expansion (Sharma, 1951).

2. Experimental Procedure

For the determination of the photoelastic constants of barite, the well-known method of Pockels (1889) was adopted. This consisted of two sets of measurements, namely (1) the determination of the relative retardation of the polarised components for various directions of stress and of observation, and (2) the determination of the absolute path retardation of the two polarised components in every case. The absolute path retardation for light polarised either parallel or perpendicular to the direction of pressure was

measured by getting the interference pattern between the two sides of the specimen and finding the load necessary for a shift of one fringe (Ramachandran, 1947).

Six specimens of different orientations were cut and polished from a transparent flawless piece of barite. They were in the form of rectangular prisms. The specimens used for final measurements on relative retardation had the dimensions and orientations given in Table I. For the absolute retardation measurements, the thickness of each specimen was reduced to about 0·275 cm. in all the cases, to get the interference pattern between the two sides.

TABLE I

Prism No.	Length		Breadth		Thickness	
	mm.	Parallel to	mm.	Parallel to	mm.	Parallel to
I	8·30	[100]	2·78	[010]	3·64	[001]
II	6·37	[010]	4·055	[001]	3·80	[100]
III	7·09	[001]	3·80	[010]	4·04	[100]
IV	4·82	[110]	2·745	[001]	2·755	$[1\bar{1}0]$
V	6·775	[011]	3·97	[100]	3·825	$[0\bar{1}1]$
VI	8·70	[101]	3·665	[010]	2·75	$[10\bar{1}]$

The details of the experimental technique are not described here as they are essentially the same as those used by Ramachandran (1947) and Bhagavantam and Suryanarayana (1947–49). No lever arrangement was employed for the compression of the crystals, but the apparatus used was similar to the one used by Ramachandran for the determination of the photoelastic constants of diamond. The direction of the pressure was always parallel to the length of the prism and observations were made perpendicular to both the lateral sides. To uniformise the pressure, 2 mm. thick lead washers were used on both sides of the prism. As the length of the prisms were roughly two to three times their lateral dimensions, the stress in the central portion was practically constant. The crystals were subjected to a maximum stress of 150 Kg/cm.^{2} and were found to return to their original state of birefringence when the stress was removed. Initially a large stress was applied so that the specimen sunk a little into the lead. This procedure helped to keep the orientation of the specimen fixed for further measurements.

Following Pockels, all the measurements were carried out at the middle of the length of the prism at three different places along its breadth, namely the right edge, the middle and the left edge. For the determination of relative path retardation, a Fuess Babinet compensator was employed to analyse the ellipticity of the light emerging from the crystal. In this case, measurements were carried out for incident light polarised both at $+45°$ and at $-45°$ to the vertical and an average was taken of these two sets of readings. Even if the pressure applied is not exactly in the vertical direction, the average reading will give the correct value.

3. Theoretical Considerations

Since the notation of the general theory of photoelasticity for the case of the orthorhombic system will have to be used often, it will be useful to give a brief resumé of the results here.

As the various other properties like elasticity, etc., are always expressed with reference to the crystallographic axes, the same has been used as the reference system in the following. Accordingly, for the case of barite, the three principal refractive indices for λ 5893 Å are

$$n_x = 1{\cdot}6481, \quad n_y = 1{\cdot}6372, \quad n_z = 1{\cdot}6361.$$

It is assumed that Fresnel's laws hold in a homogeneously deformed crystal and that the difference between the optical parameters of the crystal in the deformed and the original states are linear functions of the deformation components, or the stress components. Thus for the case of the orthorhombic system,

$$\begin{aligned}
a_{11} - a_{11}^0 &= -(q_{11}X_x + q_{12}Y_y + q_{13}Z_z) \\
a_{22} - a_{22}^0 &= -(q_{21}X_x + q_{22}Y_y + q_{23}Z_z) \\
a_{33} - a_{33}^0 &= -(q_{31}X_x + q_{32}Y_y + q_{33}Z_z) \\
a_{23} &= -q_{44}Y_z; \quad a_{31} = -q_{55}Z_x; \quad a_{12} = -q_{66}X_y. \qquad (1)
\end{aligned}$$

or

$$\begin{aligned}
a_{11} - a_{11}^0 &= p_{11}x_x + p_{12}y_y + p_{13}z_z \\
a_{22} - a_{22}^0 &= p_{21}x_x + p_{22}y_y + p_{23}z_z \\
a_{33} - a_{33}^0 &= p_{31}x_x + p_{32}y_y + p_{33}z_z \\
a_{23} &= p_{44}y_z; \quad a_{31} = p_{55}z_x; \quad a_{12} = p_{66}x_y \qquad (2)
\end{aligned}$$

Here a_{kk} and a^0_{kk} are the optical polarisation constants of the crystal in the deformed and undeformed states respectively. The first group of constants q_{ij} are called the piezo-optic constants, while the second group p_{ij} are the elasto-optic constants. They are related to each other by the relations

$$p_{ij} = \sum_{k=1}^{6} q_{ik} \cdot c_{kj}; \quad q_{ij} = \sum_{k=1}^{6} p_{ik} \cdot s_{kj} \tag{3}$$

where $c_{ik} = c_{ki}$ and $s_{ik} = s_{ki}$ are the elastic constants and elastic moduli respectively. For the orthorhombic system, these are connected with each other by the relations

$$\begin{aligned} x_x &= -\{s_{11}X_x + s_{12}Y_y + s_{13}Z_z\} \\ y_y &= -\{s_{12}X_x + s_{22}Y_y + s_{23}Z_z\} \\ z_z &= -\{s_{13}X_x + s_{23}Y_y + s_{33}Z_z\} \\ y_z &= -s_{44}Y_z; \quad z_x = -s_{55}Z_x; \quad x_y = -s_{66}X_y. \end{aligned} \tag{4}$$

Also the linear dilatation in a direction 'm' is given by the following equation

$$\begin{aligned} \frac{t'-t}{t} = {} & x_x \cos^2(m, x) + y_y \cos^2(m, y) + z_z \cos^2(m, z) + \\ & + y_z \cos(m, y) \cos(m, z) + z_x \cos(m, z) \cos(m, x) \\ & + x_y \cos(m, x) \cos(m, y) \end{aligned} \tag{5}$$

Where t' and t are the thicknesses in the direction 'm' in the deformed and undeformed states, and $\cos(m, x)$ represents the cosine of the angle between the X-axis and the direction 'm'.

Now let us consider the case of prism I. Here the pressure is acting along the X-axis. Hence all the pressure components except X_x are zero, *i.e.*, $P_x = X_x$. Thus equation (1) becomes

$$\begin{aligned} a_{11} - a_{11}^0 &= -q_{11}P_x \\ a_{22} - a_{22}^0 &= -q_{21}P_x \\ a_{33} - a_{33}^0 &= -q_{31}P_x. \end{aligned} \tag{6}$$

The equation for the path retardation on compression, for light vibrating parallel to the direction of pressure, when the direction of observation is along the Z-axis can be derived as follows.

Then $a_{11}^0 = \frac{1}{n_x^2}$, n_x being the corresponding refractive index. Differentiating this we have

$$\Delta a_{11}^0 = -\frac{2}{n_x^3} \cdot \Delta n_x \tag{7}$$

From (6) and (7) one obtains

$$\Delta n_x = \frac{n_x^3 q_{11} P_x}{2}. \tag{8}$$

For the case of fringes of equal thickness due to interference between light reflected from the front and back surfaces of the specimen, the differential path retardation resulting from the applied stress will be equal to

$$\Delta (2n_x \cdot t) = 2n_x \cdot \Delta t + 2t \cdot \Delta n_x$$

This is also equal to λ, the wavelength of light employed, if a shift of one fringe is observed. Thus

$$\lambda = 2n_x \cdot \Delta t + 2t \cdot \Delta n_x \tag{9}$$

Here Δn_x, the change in the refractive index due to compression is given by equation, (8) and Δt, the change in thickness in the direction of observation (Z), can be got from equation (4), and this is equal to $\Delta t = -P_x t s_{13}$. Substituting these values in (9),

$$\frac{\lambda}{P_x^{\parallel} \cdot t} = n_x^3 q_{11} - 2n_x \cdot s_{13}. \tag{10}$$

Here $P_x^{\parallel}$ is the pressure expressed in dynes/cm.^{2} that is necessary to bring about one fringe shift and is to be taken as positive for compression. Thus the left-hand side of the equation (10) gives the path retardation introduced by a unit pressure of 1 dyne/cm.^{2} for a thickness of 1 cm., when the direction of vibration of light is parallel to that of pressure.

Similarly, for light with vibration directions normal to the pressure, we have

$$\frac{\lambda}{P_x^{\perp} \cdot t} = n_y^3 q_{21} - 2n_y s_{13}, \tag{11}$$

where $P_x^{\perp}$ has the same significance as P_x. From equations (10) and (11), the expression for the relative retardation on compression between the two rays vibrating parallel and normal to the direction of pressure, can be obtained. However one should take into effect the fact that in this case the light is traversing the crystal only once, whereas in the case of the absolute retardation measurements, it is traversing the crystal two times. Thus we have for the path retardation introduced by a unit pressure of 1 dyne/cm.^{2}, for a thickness of 1 cm.,

$$\frac{\lambda}{2t}\left[\frac{1}{P_x^{\parallel}} - \frac{1}{P_x^{\perp}}\right] = \tfrac{1}{2}(n_x^3 q_{11} - n_y^3 q_{21}) + s_{13}(n_y - n_x) \tag{12}$$

Similar equations can be derived for the other pressure and observation directions. The equations so obtained are given in Table II. The fifth column in the table denotes the nature of the observation, thereby indicating whether the observation made is absolute retardation or relative retardation

TABLE II

No.	No. of Prism	Direction of pressure parallel to	Direction of observation parallel to	Nature of observation	Theoretical expression for path retardation, Δ	Observed value of Δ
1	I	[100]	[001]	absolute (P)	$(n_x^3 q_{11} - 2n_x s_{13})$	$9{\cdot}00\times10^{-13}$
2	I	[100]	[001]	absolute (N)	$(n_y^3 q_{21} - 2n_y s_{13})$	$15{\cdot}52\times10^{-13}$
3	I	[100]	[001]	relative	$\frac{1}{2}(n_x^3 q_{11} - n_y^3 q_{21}) + s_{13}(n_y - n_x)$	$-3{\cdot}22\times10^{-13}$
4	I	[100]	[010]	relative	$\frac{1}{2}(n_x^3 q_{11} - n_z^3 q_{31}) + s_{12}(n_z - n_x)$	$-1{\cdot}02\times10^{-13}$
5	II	[010]	[100]	absolute (P)	$(n_y^3 q_{22} - 2n_y s_{12})$	$39{\cdot}76\times10^{-13}$
6	II	[010]	[100]	absolute (N)	$(n_z^3 q_{32} - 2n_z s_{12})$	$35{\cdot}26\times10^{-13}$
7	II	[010]	[100]	relative	$\frac{1}{2}(n_y^3 q_{22} - n_z^3 q_{32}) + s_{12}(n_z - n_y)$	$1{\cdot}19\times10^{-13}$
8	II	[010]	[001]	relative	$\frac{1}{2}(n_y^3 q_{22} - n_x^3 q_{12}) + s_{23}(n_x - n_y)$	$-4{\cdot}66\times10^{-13}$
9	III	[001]	[100]	absolute (P)	$(n_z^3 q_{33} - 2n_z s_{13})$	$21{\cdot}16\times10^{-13}$
10	III	[001]	[100]	absolute (N)	$(n_y^3 q_{23} - 2n_y s_{13})$	$13{\cdot}44\times10^{-13}$
11	III	[001]	[100]	relative	$\frac{1}{2}(n_z^3 q_{33} - n_y^3 q_{23}) + s_{13}(n_y - n_z)$	$2{\cdot}91\times10^{-13}$
12	III	[001]	[010]	relative	$\frac{1}{2}(n_z^3 q_{33} - n_x^3 q_{13}) + s_{23}(n_x - n_z)$	$2{\cdot}38\times10^{-13}$
13	IV	[110]	$[1\bar{1}0]$	relative	$\frac{n_{xy}^3}{8}(q_{11}+q_{12}+q_{21}+q_{22}+2q_{66}) - \frac{n_z^3}{4}(q_{31}+q_{32}) + \frac{1}{4}(s_{11}+2s_{12}+s_{22}-s_{66})(n_z - n_{xy})$	$3{\cdot}67\times10^{-13}$
14	V	[011]	$[0\bar{1}1]$	relative	$\frac{n_{yz}^3}{8}(q_{22}+q_{23}+q_{32}+q_{33}+2q_{44}) - \frac{n_x^3}{4}(q_{12}+q_{13}) + \frac{1}{4}(s_{22}+2s_{23}+s_{33}-s_{44})(n_x - n_{yz})$	$-2{\cdot}32\times10^{-13}$
15	VI	[101]	$[10\bar{1}]$	absolute (P)	$\frac{n_{xz}^3}{4}(q_{31}+q_{33}+q_{11}+q_{13}+2q_{55}) - \frac{n_{xz}}{2}(s_{11}+2s_{13}+s_{33}-s_{55})$	$14{\cdot}55\times10^{-13}$
16	VI	[101]	$[10\bar{1}]$	absolute (N)	$\frac{n_y^3}{2}(q_{21}+q_{23}) - \frac{n_y}{2}(s_{11}+2s_{13}+s_{33}-s_{55})$	$15{\cdot}97\times10^{-13}$

Here n_{xy}, n_{yz}, n_{xz} are given by the following expression :

$$\frac{1}{n_{ij}^2} = \frac{1}{2}\left(\frac{1}{n_i^2} + \frac{1}{n_j^2}\right), \quad [i, j = x, y, z]$$

measurement and also, in the former case, whether the light is vibrating parallel to the direction of pressure (P) or normal to it (N).

4. Results

The path retardations Δ introduced by a pressure of 1 dyne/cm.^{2} for λ 5893, when the thickness of the crystal along which the light is traversing is 1 cm., are also entered in the last column of Table II, for the various directions of observation and pressure.

The elastic constants of barite have been determined by Voigt (1888) by the static method and later by Bergmann (1935) by the ultrasonic diffraction pattern method. Their values are given in Tables III and IV. The mean of these two sets of values have been used in this paper for determining the change in thickness of the prism, as well as for evaluating the elasto-optic coefficients. Recently, Seshagiri Rao (1951) has also measured the elastic constants of barite using the wedge method (Bhagavantam and Bhimasenachar, 1944). His values do not differ much from the mean values used in this paper except for c_{23} and s_{23}.

Table III

	c_{11}	c_{22}	c_{33}	c_{44}	c_{55}	c_{66}	c_{12}	c_{23}	c_{13}
Voigt ..	8·83	7·85	10·50	1·18	2·85	2·75	4·51	2·65	2·65
Bergmann ..	8·83	7·81	10·38	1·17	2·80	2·55	4·77	2·89	2·69
Values used by the author	8·83	7·83	10·44	1·175	2·825	2·65	4·64	2·77	2·67

All the constants are given in units of 10^{11} dynes/cm.^{2}

	s_{11}	s_{22}	s_{33}	s_{44}	s_{55}	s_{66}	s_{12}	s_{23}	s_{13}
Voigt ..	16·4	18·9	10·6	84·0	34·8	36·0	−9·0	−1·9	−2·5
Bergmann ..	17·2	19·9	10·9	85·5	35·8	39·2	−9·9	−1·7	−3·0
Values used by author	16·8	19·4	10·75	84·75	35·3	37·6	−9·45	−1·8	−2·75

All the constants are given in units of 10^{-13} cm.^{2} dyne^{-1}.

Using these values of the elastic constants, the piezo-optic constants can be obtained from the equations for the absolute path retardation given in Table II. The measurements on the relative retardation provide a check on the absolute measurements. However it must be mentioned

here that in the measurements on absolute path retardation, a change in the load of 3 to 5% will just escape notice as the fringe width was actually about 1/5 mm. As the major contribution to the path retardation in almost all the cases is due to the change in thickness of the specimen, the quantity that is actually sought, *i.e.*, the path retardation due to the change in refractive index is obtained as a small difference between two large quantities. Thus one finds, that in some cases, the values obtained from the relative retardation method vary by even as much as 50% from the corresponding values obtained from the absolute retardation measurements. Hence in such cases the absolute retardation method was used to give the sum of the two piezo-optic coefficients and the relative retardation experiments to give the difference between the two. From these, the absolute values were determined and are given below.

For prisms IV, V, and VI, no absolute retardation measurement is necessary to determine the values of q_{44}, q_{55} and q_{66}, as can be seen from the theoretical expressions given in Table II. However for prism VI, as the Babinet fringe shift was extremely small even with the maximum load of 150 Kg/mm.^{2}, the absolute retardation technique was made use of for the determination of q_{55}.

The values of the piezo-optic coefficients of barite expressed in units of 10^{-13} cm.^{2} dyne^{-1} are given below:

$q_{11} = -0{\cdot}079$	$q_{44} = 0{\cdot}20$	$q_{12} = 3{\cdot}81$	$q_{23} = 1{\cdot}23$
$q_{22} = 1{\cdot}77$	$q_{55} = -0{\cdot}435$	$q_{13} = 1{\cdot}64$	$q_{31} = 0{\cdot}44$
$q_{33} = 2{\cdot}56$	$q_{66} = 1{\cdot}39$	$q_{21} = 1{\cdot}49$	$q_{32} = 1{\cdot}23$

The values of the elasto-optic coefficients calculated from the values of the piezo-optic coefficients and the elastic constants using equation (3) are given below:

$p_{11} = 0{\cdot}21$	$p_{44} = 0{\cdot}002$	$p_{12} = 0{\cdot}25$	$p_{23} = 0{\cdot}19$
$p_{22} = 0{\cdot}24$	$p_{55} = -0{\cdot}012$	$p_{13} = 0{\cdot}16$	$p_{31} = 0{\cdot}275$
$p_{33} = 0{\cdot}31$	$p_{66} = 0{\cdot}037$	$p_{21} = 0{\cdot}34$	$p_{32} = 0{\cdot}22$

5. Discussion of Results

It is clear from the results given above that the elasto-optic constants p_{hk} ($h, k = 1, 2, 3$) of barite are of the same order of magnitude and are considerably larger than p_{44}, p_{55} and p_{66}. Similar observations have been recorded in the case of other ionic crystals like NaCl, KCl, etc. But in the case of covalent crystals like magnesium oxide, diamond and topaz (Burstein

and Smith, 1948; Ramachandran, 1950; Eppendahl, 1920) such a disparity between the values of p_{44}, p_{55}, p_{66} and the other elasto-optic constants do not exist. In other words, for covalent crystals all the elasto-optic constants are found to be of nearly the same value. Moreover, the piezo-optic and elasto-optic constants of barite are found to be higher than those of topaz. The piezo-optic constants of topaz are found to be extremely small as in the case of diamond.

It must be mentioned here, that the accuracy of the values of the elastic constants of barite, especially of s_{12}, s_{23} and s_{13} plays a very important role in the calculation of the values of the photoelastic constants. As mentioned before, the major contribution to the path retardation is due to the change in thickness of the specimen. Especially in the case of Prism I, with direction of observation parallel to Z, and for light with vibration direction normal to the direction of strain, it was found that more than 95% of the retardation observed was due to the change in thickness. Naturally an error of 1% in the value of the elastic constant (s_{13}, in this particular case) is enough to upset the values of the photoelastic constants completely, although the order of magnitude will not be affected.

Now let us consider the behaviour of barite, under uniform hydrostatic pressure. The six pressure components can then be written as

$$X_x = Y_y = Z_z = P. \quad X_y = Z_x = Y_z = 0$$

Hence the equation for the polarisation constants becomes from (10)

$$a_{11} - a_{11}^0 = -P\{q_{11} + q_{12} + q_{13}\}$$
$$a_{22} - a_{22}^0 = -P\{q_{21} + q_{22} + q_{23}\}$$
$$a_{33} - a_{33}^0 = -P\{q_{31} + q_{32} + q_{33}\}$$

Introducing the numerical values of the piezo-optic constants we get

$$\omega_x^2 - \omega_x^{0^2} = -5{\cdot}37 \times 10^{-13}.P$$
$$\omega_y^2 - \omega_y^{0^2} = -4{\cdot}49 \times 10^{-13}.P$$
$$\omega_z^2 - \omega_z^{0^2} = -4{\cdot}23 \times 10^{-13}.P. \qquad (13)$$

Here the polarisation constants have been replaced by the square of the velocity of propagation of light. The superscript 0 has the same significance as before. Thus, from equation (13), it is seen that all the principal velocities undergo a small reduction. In other words, all the principal refractive indices increase under the influence of hydrostatic pressure.

The change in double refraction due to uniform hydrostatic pressure can be had from

$$(\omega_z^2 - \omega_x^2) - (\omega_z^{0\,2} - \omega_x^{0^2}) = -\,P\,(q_{31} + q_{32} + q_{33} - q_{11} - q_{12} - q_{13})$$
$$= 1{\cdot}14 \times 10^{-13}.P$$

Hence

$$(n_x - n_z) - (n_x^0 - n_z^0) = \frac{n_{xz}^3}{2}\,[(\omega_z^2 - \omega_x^2) - (\omega_z^{0^2} - \omega_x^{0^2})]$$
$$= 2{\cdot}54 \times 10^{-13}.P$$

Thus under such circumstances, the birefringence increases. The magnitude of the optic axial angle (2Ω) is given by

$$\sin \Omega = \sqrt{\frac{\omega_x^2 - \omega_y^2}{\omega_z^2 - \omega_z^2}}$$

From (13), for barite

$$\omega_x^2 - \omega_y^2 = \omega_x^{0^2} - \omega_y^{0^2} - 0{\cdot}885 \times 10^{-13}.P$$
$$\omega_x^2 - \omega_z^2 = \omega_x^{0^2} - \omega_z^{0^2} - 1{\cdot}143 \times 10^{-13}.P.$$

Since the denominator is increased to a greater extent than the numerator, the binormal angle decreases under the influence of a hydrostatic pressure.

Let us now consider the influence of temperature on the three principal refractive indices. Recently Radhakrishnan (1951) has determined the temperature-coefficients of all the three indices of barite. His results are:

$$\frac{dn_x}{dt} = -\,2{\cdot}49 \times 10^{-5};\quad \frac{dn_y}{dt} = -\,1{\cdot}79 \times 10^{-5};\quad \frac{dn_z}{dt} = -2{\cdot}11 \times 10^{-5} \qquad (14)$$

As is well known, the temperature dependence of the three principal refractive indices is determined partly by the deformation following the temperature change and partly by the direct influence of temperature on the refractive indices (Pockels, 1889). This can be written symbolically as

$$\frac{dn}{dt} = \left(\frac{dn}{dt}\right) + \frac{\partial n}{\partial t} \qquad (15)$$

where $\frac{dn}{dt}$ is the experimentally observed value of the temperature coefficient, $\left(\frac{dn}{dt}\right)$ the factor due to thermal dilatation and $\frac{\partial n}{\partial t}$ is the true temperature coefficient of refractive index.

The temperature coefficient $\left(\frac{dn}{dt}\right)$ due to thermal dilatation can be calculated from the known linear thermal expansion and the known elasto-optic constants. For barite, Sharma (1951) finds for the thermal expansion coefficients along the three principal axes the values $\alpha_1 = 13{\cdot}98 \times 10^{-6}$, $\alpha_2 = 24{\cdot}30 \times 10^{-6}$, $\alpha = 14{\cdot}53 \times 10^{-6}$. From these

$$\left(\frac{dn_x}{dt}\right) = -2{\cdot}538 \times 10^{-5}$$

$$\left(\frac{dn_y}{dt}\right) = -2{\cdot}931 \times 10^{-5}$$

$$\left(\frac{dn_z}{dt}\right) = -2{\cdot}989 \times 10^{-5} \qquad (16)$$

Thus from (14) and (15) the true temperature coefficients are given by

$$\frac{\partial n_x}{\partial t} = +0{\cdot}05 \times 10^{-5}$$

$$\frac{\partial n_y}{\partial t} = +1{\cdot}14 \times 10^{-5}$$

$$\frac{\partial n_z}{\partial t} = +0{\cdot}88 \times 10^{-5}$$

It is seen that all the true temperature coefficients are positive as is to be expected. Also the value $\frac{\partial n_y}{\partial t}$ is much larger than $\frac{\partial n_x}{\partial t}$ and $\frac{\partial n_z}{\partial t}$. Such a behaviour is to be expected when we consider the fact that even though Sharma reports a maximum dilatation along the Y axis, Radhakrishnan finds a minimum temperature coefficient of refractive index along that axis.

In conclusion the author's thanks are due to Professor R. S. Krishnan for his constant interest and kind encouragement during the progress of this work and to Dr. G. N. Ramachandran for the discussions he had with him.

6. Summary

All the 12 elasto-optic constants of barite have been determined and the values obtained for λ 5893 are

$p_{11} = 0{\cdot}21$	$p_{44} = 0{\cdot}002$	$p_{12} = 0{\cdot}25$	$p_{23} = 0{\cdot}19$
$p_{22} = 0{\cdot}24$	$p_{55} = -0{\cdot}012$	$p_{13} = 0{\cdot}16$	$p_{31} = 0{\cdot}275$
$p_{33} = 0{\cdot}31$	$p_{66} = 0{\cdot}037$	$p_{21} = 0{\cdot}34$	$p_{32} = 0{\cdot}22$

The behaviour of the optical properties of barite on uniform compression on all sides is discussed. The true temperature coefficients of the three principal refractive indices have also been calculated.

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γ-SUBSTITUTION IN THE RESORCINOL NUCLEUS

Part X. Nuclear Benzylation of Methyl β-Resorcylate

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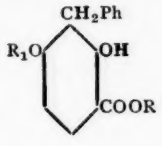
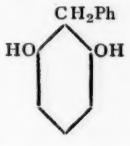
2-BENZYLRESORCINOL was required in connection with the work described in the accompanying paper. As it was unknown, possible methods for its synthesis were investigated. 2-Alkylresorcinols in general, can be prepared by the method of Robinson and Shah,[1] by nuclear alkylation of methyl β-resorcylate to 4-O-alkyl-3-alkyl derivative, which on subsequent dealkylation, hydrolysis and decarboxylation would give 2-alkylresorcinol.

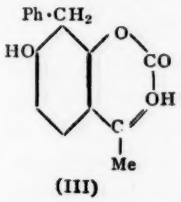
Methyl β-resorcylate, when treated with benzyl chloride in methanolic potassium hydroxide gave methyl -2-hydroxy-3-benzyl-4-benzyloxybenzoate (I, R = Me, $R_1 = CH_2Ph$). It was debenzylated by concentrated hydrochloric acid to methyl -2: 4-dihydroxy-3-benzylbenzoate (I, R = Me, $R_1 = H$). The latter was hydrolysed by alkali to 2: 4-dihydroxy-3-benzylbenzoic acid (I, $R = R_1 = H$), which was then decarboxylated by heating with copper in quinoline to get 2-benzylresorcinol (II).



(I)



(II)



(III)

For comparison it was also prepared by Clemmensen reduction of 2-benzoylresorcinol.[2]

2-Benzylresorcinol (II) was characterised by preparing its diacetyl, dibenzoyl and dibromo derivatives. On condensation with phthalic anhydride in presence of concentrated sulphuric acid, it gave a product which from its properties, appears to be a homologue of fluorescein.

It easily underwent Pechmann condensation with ethyl acetoacetate in presence of concentrated sulphuric acid to give 7-hydroxy-4-methyl-8-benzylcoumarin (III), which was also obtained by the Clemmensen reduction of

7-hydroxy-4-methyl-8-benzoylcoumarin. Attempts at nuclear benzylation of 7-hydroxy-4-methylcoumarin, to get the above compound, resulted in a failure and only 7-benzyloxy-4-methylcoumarin was formed.

Experimental

Nuclear Benzylation of Methyl β-Resorcylate: Methyl -2-Hydroxy-3-benzyl-4-benzyloxybenzoate (*I*, $R = Me$, $R_1 = CH_2Ph$)

To a methanolic solution of potassium hydroxide (8·4 g. in 50 c.c.), methyl β-resorcylate (8·4 g.) and benzyl chloride (19·0 g.) were added, and the mixture left overnight. Next day the reaction mixture was refluxed for 6 hours, methanol was distilled off and excess of benzyl chloride was removed by steam-distillation. The residue was extracted with ether and the ether extract washed with sodium hydroxide solution (10%). On removing the ether an oily product was obtained, which was washed with petroleum ether. The solid product, thus obtained was crystallised from alcohol when colourless needles of *methyl -2-hydroxy-3-benzyl-4-benzyloxybenzoate* (*I*, $R = Me$, $R_1 = CH_2Ph$) separated, m.p. 100-01° (1·2 g.) (Found: C, 76·2; H, 5·5. $C_{22}H_{20}O_4$ requires C, 75·9; H, 5·7%). It is insoluble in alkali and gives a deep violet coloration with alcoholic ferric chloride.

Debenzylation of Methyl -2-hydroxy-3-benzyl-4-benzyloxybenzoate (*I*, $R = Me$, $R_1 = CH_2Ph$): *Methyl 2:4-Dihydroxy-3-benzylbenzoate* (*I*, $R = Me$, $R_1 = H$)

A mixture of methyl -2-hydroxy-3-benzyl-4-benzyloxybenzoate (4·0 g.) and concentrated hydrochloric acid (50 c.c.) in glacial acetic acid (100 c.c.) was refluxed for 2 hours. After removing acetic acid and benzyl alcohol by steam distillation, the product obtained was boiled in benzene with activated charcoal. On concentrating the benzene solution pale yellow rhombic crystals were obtained. On recrystallising from alcohol, colourless crystals of *methyl -2:4-dihydroxy-3-benzylbenzoate* (*I*, $R = Me$, $R_1 = H$) were obtained, m.p. 129-30° (0·6 g.) (Found: C, 69·5; H, 5·4. $C_{15}H_{14}O_4$ requires C, 69·8; H, 5·4%).

Hydrolysis of Methyl 2:4-Dihydroxy-3-benzylbenzoate (*I*, $R = Me$, $R_1 = H$): *2:4-Dihydroxy-3-benzylbenzoic Acid* (*I*, $R = R_1 = H$)

Methyl 2:4-dihydroxy-3-benzylbenzoate (I, R = Me, $R_1 = H$) (2·5 g.) was dissolved in sodium hydroxide solution (10%) and allowed to stand for 48 hours. The solid obtained on acidification was crystallised from

dilute alcohol when 2:4-*dihydroxy*-3-*benzylbenzoic acid* (*I*, $R = R_1 = H$) separated in colourless needles, m.p. 84–85° (1·2 g.) (Found: C, 68·5; H, 4·8. $C_{14}H_{12}O_4$ requires C, 68·9; H, 4·9%).

Decarboxylation of 2:4-*Dihydroxy*-3-*benzylbenzoic Acid* (*I*, $R = R_1 = H$): 2-*Benzylresorcinol* (*II*)

To a solution of 2:4-dihydroxy-3-benzylbenzoic acid (I, $R = R_1 = H$) (0·1 g.) in quinoline (5 c.c.), copper powder (0·1 g.) was added and the mixture heated at 180° for 1 hour. Copper was filtered and washed with ether. The filtrate was treated with dilute hydrochloric acid and extracted with ether. The ether extract was washed with sodium bicarbonate and then with water and dried. 2-*Benzylresorcinol* was obtained on removal of the ether, and was found to be identical with the product described below.

Clemmensen Reduction of 2-*Benzoylresorcinol*: 2-*Benzylresorcinol* (*II*)

2-Benzoylresorcinol[3] (10·0 g.) was mixed with zinc amlagam (prepared from zinc, 20·0 g., and mercuric chloride, 1·0 g.) and dilute hydrochloric acid (1:1; 25 c.c.) was added to it. The reaction mixture was heated on a steam-bath. At intervals of half an hour, more of dilute hydrochloric acid (1:1) was added and heating continued till the reaction mixture gave no coloration with alcoholic ferric chloride. The supernatant liquid was decanted and extracted with ether. On removal of ether it gave an oily product which when distilled under reduced pressure (230–40°/30 mm.) gave 2-benzylresorcinol, m.p. 82–84° (6·0 g.) (Found: C, 77·6; H, 5·7. $C_{13}H_{12}O_2$ requires C, 78·0; H, 6·0%).

Diacetyl derivative was prepared by acetic anhydride and pyridine method and was crystallised from rectified spirit, m.p. 79–80° (Found: C, 71·6; H, 5·5. $C_{17}H_{16}O_4$ requires C, 71·8; H, 5·6%).

Dibenzoyl derivative was prepared by benzoyl chloride and pyridine method, and was crystallised from rectified spirit in small pale yellow needles, m.p. 138–39° (Found: C, 79·3; H, 5·3. $C_{27}H_{20}O_4$ requires C, 79·4; H, 4·9%).

Dibromo derivative was prepared by bromination (3 mols. of bromine) in carbon disulphide and was crystallised from dilute alcohol, colourless plates, m.p. 127–28° (Found: Br, 44·8. $C_{13}H_{10}O_2Br_2$ requires Br, 44·7%).

Pechmann Condensation of 2-*Benzylresorcinol with Ethyl Acetoacetate*: 7-*Hydroxy*-4-*methyl*-8-*benzylcoumarin* (*III*)

2-Benzylresorcinol (1·0 g.) was dissolved in ethyl acetoacetate (1·2 g.), concentrated sulphuric acid (4 c.c.) was added to it and kept overnight.

The next day it was poured on crushed ice and the solid obtained was crystallised from dilute alcohol when *7-hydroxy-4-methyl-8-benzylcoumarin* (III) separated, m.p. 238° (0·8 g.) (Found: C, 76·9; H, 5·1. $C_{11}H_{14}O_3$ requires C, 76·7; H, 5·3%). It dissolves in alkali giving strong blue fluorescence.

Clemmensen Reduction of 7-Hydroxy-4-methyl-8-benzoylcoumarin : 7-Hydroxy-4-methyl-8-benzylcoumarin (III)

7-Hydroxy-4-methyl-8-benzoylcoumarin[3] (5·0 g.) and zinc amalgam from (10·0 g. zinc) in hydrochloric acid (1 : 1; 40 c.c.) were heated on a steam-bath, extra hydrochloric being added at intervals and heating continued till a drop of the reaction mixture gave no coloration with alcoholic ferric chloride. At the end of the reaction, the supernatant liquid was decanted when hot. On cooling crystals of 7-hydroxy-4-methyl-8-benzylcoumarin (III) were deposited, recrystallised from dilute alcohol, m.p. and mixed m.p. 238° (2·1 g.).

Attempted Nuclear Benzylation of 7-Hydroxy-4-methylcoumarin

A mixture of 7-hydroxy-4-methylcoumarin (5·9 g.), anhydrous potassium carbonate (6·3 g.) and benzyl chloride (12·6 g.) in dry acetone (25 c.c.) was kept overnight. The next day, it was refluxed for 6 hours. Excess of acetone and benzyl chloride were removed. The residue was washed with dilute sodium hydroxide (1 N) and the insoluble product after washing with water was collected and crystallised from rectified spirit, colourless needles, m.p. 118–20° (3 g.). It was identified as 7-benzyloxy-4-methylcoumarin. Bridge, Crodes, Cubin and Robertson give m.p. 117–5°.

Benzylation of Methyl β-Resorcylate : Methyl 2-Hydroxy-4-benzyloxybenzoate

A mixture of methyl β-resorcylate (4·2 g.), benzyl chloride (12·6 g.) and anhydrous potassium carbonate (6·3 g.) in dry acetone (25 c.c.) was refluxed for 8 hours. Acetone was distilled off and benzyl chloride was removed by steam distillation. The product obtained was crystallised from rectified spirit, when *methyl -2-hydroxy-4-benzyloxybenzoate* separated in colourless needles, m.p. 102–04° (4·1 g.) (Found: C, 69·6; H, 5·5. $C_{15}H_{14}O_4$ requires C, 69·8; H, 5·4%).

Summary

Two syntheses of 2-benzylresorcinol are described. Methyl β-resorcylate on nuclear benzylation gave methyl 2-hydroxy-3-benzyl-4-benzyloxybenzoate which on successive debenzylation, hydrolysis and decarboxylation gave

2-benzylresorcinol. It has also been prepared by the Clemmensen's reduction of 2-benzoylresorcinol. 2-Benzylresorcinol on Pechmann condensation with ethyl acetoacetate gave 7-hydroxy-4-methyl-8-benzylcoumarin. The latter was also obtained by Clemmensen's reduction of 7-hydroxy-4-methyl-8-benzoylcoumarin.

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CHEMOTHERAPY OF MALARIA

V. Synthesis of 4-(Thiazolylamino)-Quinolines and 4-Phenoxyquinolines

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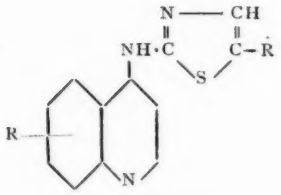
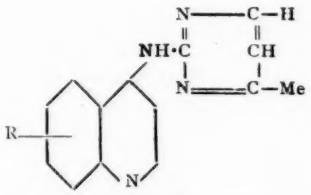
As an extension of the work reported in the previous parts, this paper records the synthesis of some derivatives of 4-amino-quinolines wherein the amino group bears a thiazole and pyrimidine ring as a substituent. It should be noted that in such compounds of formula (I) and (II), the significant groups —NH—C(=S)—N— and —NH—C(=N)—N— are present.



(I)



(II)

Compounds of type (I) can be synthesised by condensing 4-thiocarbamido-quinolines with halogenoketones according to the standard procedure of preparing thiazoles, but as was indicated in Part III, the starting thiocarbamido derivatives could not be prepared. Since we have also found that the amino group in the 4-aminoquinolines is very inert, the only method of preparing the compounds of formula (I) consisted in the condensation of 4-chloro-quinolines with the 2-aminothiazoles. Such a condensation could not be effected by boiling the constituents in alcohol but the reaction proceeded when conducted in phenol medium. Thus the amino group in thiazoles resemble the aliphatic amino rather than the aromatic amino groups.

The general procedure adopted to condense 4-chloroquinolines with 2-aminothiazoles in phenol medium was to heat the mixture at 150-60° for three to six hours and then pour the cooled mixture into dilute alkali solution. The yields of the condensation products were about 40 to 50% in the case of the quinolines while with the quinaldines, the yields were less and the

products were also difficult to purify. Thus, 4:7-dichloroquinoline was reacted in turn with 2-aminothiazole, 2-amino-5-ethylthiazole and 2-amino-5-isopropylthiazole to furnish respectively 4-(thiazolyl-2′-amino)-7-chloroquinoline (I, R = 7 — Cl; R′ = H), 4-(5′-ethylthiazolyl-2′-amino)-7-chloroquinoline (I, R = 7—Cl; R′ = C_2H_5) and 4-(5′-isopropylthiazolyl-2′-amino-7-chloroquinoline (I, R = 7—Cl; R′ = $CHMe_2$). Similarly, 4-chloro-8-methoxyquinaldine, 4-chloro-6-methoxyquinaldine and 4:6-dichloroquinaldine were each reacted in turn with 2-amino-thiazole, 2-amino-5-ethylthiazole and 2-amino-5-isopropylthiazole to obtain the corresponding thiazolylaminoquinoline derivatives of formula (I) in most cases. The condensation of 4-chloro-6-methoxy quinaldine and of 4:6-dichloroquinaldine with 2-aminothiazole in phenol medium furnished only the 4-phenoxy quinaldine derivatives instead of the thiazolylamino compounds of formula (I). On the other hand, 2-aminothiazole condensed alright with 4:7-dichloroquinoline and 4-chloro-8-methoxyquinoline furnishing the thiazolylaminoquinolines. This indicates that the reactivity of the chlorine atom in position 4 of the quinoline ring is significantly altered by the nature and position of the substituents in the quinoline ring.

Attempts to condense 2-chlorolepidine with the aminothiazoles were not successful. Refluxing the constituents in alcoholic medium did not lead to condensation while in phenol medium, only the 2-phenoxy compound was produced. This type of reduced reactivity of the chlorine atom in position 2 is not unexpected.

The condensation of 4:7-dichloroquinoline with 2-aminopyrimidine, 2-amino-4-methylpyrimidine and 2-amino-4:6-dimethylpyrimidine were tried. Refluxing the constituents in alcoholic solution led to no condensation. When they were heated in phenol medium, only a small quantity of the desired condensation product (II) was obtained when using 2-amino-4-methylpyrimidine. When the other two pyrimidines were used, no condensation product could be isolated. In these cases, 4-phenoxy-7-chloroquinoline was the other product isolated. When 2-amino-4-methyl-6-chloropyrimidine was tried, the products isolated were 4-phenoxy-7-chloropyrimidine and 2-amino-4-methyl-6-phenoxypyrimidine. When they were refluxed in amylalcohol, the quinoline was converted into 4-hydroxy-7-chloroquinoline but no condensation took place.

The above observations led us to doubt the validity of theory that the role of the phenol in the condensation is to provide first the phenoxy compound which subsequently reacts with the amines to furnish the aminoquinolines.[1] Walker,[2] on the other hand, refuses to give any importance

to the role of phenol. To study this we have prepared a number of phenoxy compounds and have studied their properties. 4-Phenoxy-7-chloroquinoline on treatment with ammonia remains unaffected; even if the phenoxy compound is suspended in phenol and ammonia passed through the hot mixture, no amino compound could be prepared. The phenoxy compound is stable to alkali and acids even on boiling. So, clearly the phenoxy compound cannot be the intermediate in the formation of the amino compounds and the role of phenol is not to furnish the phenoxy compound. We have also found that 4-phenoxy-7-chloroquinoline does not react with novaldiamine, guanidine carbonate, guanidine acetate, 2-aminopyrimidine and 2-aminothiazole. Phenol cannot be replaced by glycerol either. The role of phenol appears to be to facilitate the nucleophilic attack at the carbon atom 4 in the quinoline nucleus by the negative ion, similar to the mechanism postulated by Cutler and Surrey[3] who found that the action of acetic acid on 4:7-dichloroquinoline furnished 4-hydroxy-7-chloroquinoline.

Experimental

4-(*Thiazolyl-2'-amino*)-7-*chloroquinoline*.—An intimate mixture of 4:7-dichloroquinoline (10 g.), 2-aminothiazole (5 g.) and phenol (50 g.) was heated at 160-70° C. for 4 hours. The reaction mixture on cooling was treated with dil. sodium hydroxide (8%, 500 c.c.) and the dark red syrupy substance which was thrown out was separated, washed with little water and taken up in dil. hydrochloric acid (1:2). The acidic solution was treated with charcoal, filtered and the filtrate cooled and basified with sodium hydroxide solution (10%) whereupon the desired condensation product was obtained as a granular yellow solid. The product crystallised in needles and had m.p. 231–33° (Found: N, 16·19. $C_{12}H_8N_3SCl$ requires N, 16·06%). Picrate, m.p. 218–20°.

4-(5'-Ethylthiazolyl-2'-amino)-7-chloroquinoline.—This compound was prepared as described above from a mixture of 4:7-dichloroquinoline (5 g.), 2-amino-5-ethylthiazole (3·4 g.) and phenol (25 g.) at 145–50°. The compound crystallised from ethanol in flakes and had m.p. 236–7° (Found: N, 14·57. $C_{14}H_{12}N_3SCl$ requires N, 14·51%). Picrate, m.p. 238–40°.

4-(5'-Iso*propylthiazolyl*-2'-*amino*)-7-*chloroquinoline*.—This was prepared from 4:7-dichloroquinoline (5 g.), 2-amino-5-isopropylthiazole (3·6 g.) and phenol (25 g.) by heating the mixture at 145–50°. This compound, crystallised first from alcohol and then from acetone, separated in flakes and had m.p. 233–34° (Found: N, 13·61. $C_{15}H_{14}N_3SCl$ requires N, 13·82%). Hydrochloride, m.p. 283–5°; picrate, m.p. 249–50°.

4-(*Thiazolyl-2'-amino*)-8-*methoxyquinaldine*.—This was prepared by heating a mixture of 4-chloro-8-methoxyquinaldine (5 g.), 2-aminothiazole (2·35 g.) and phenol (25 g.) at 150–60° for 7 hours. The compound on crystallisation from a mixture of benzene and ligroin was obtained in flakes and had m.p. 207–9° (Found: N, 15·23. $C_{14}H_{13}ON_3S$ requires N, 15·50%).

4-(5'-*Ethylthiazolyl-2'-amino*)-8-*methoxyquinaldine*.—Prepared as described above, crystallised from ethanol, had m.p. 184–89° (Found: N, 14·19, $C_{16}H_{17}ON_3S$ requires N, 14·04%).

4-(5'-Iso*propylthiazolyl-2'-amino*)-8-*methoxyquinaldine*.—Prepared from a mixture of 4-chloro-8-methoxyquinaldine (5 g.), 2-amino-5-isopropylthiazole (3·1 g.) and phenol (25 g.). On crystallisation from benzene ligronin mixture, it had m.p. 202–4° (Found: N, 13·49. $C_{17}H_{19}ON_3S$ requires N, 13·41%).

4-(5'-*Ethylthiazolyl-2'-amino*)-6-*methoxyquinaldine*.—This compound prepared from a mixture of 4-chloro-6-methoxyquinaldine (5 g.), 2-amino-5-ethylthiazole (3·1 g.) and phenol (25 g.), on crystallisation from ethanol separated in pale yellow plates had m.p. 176–7° (Found: N, 13·88. $C_{16}H_{17}ON_3S$ requires N, 14·05%).

4-(5'-Iso*propylthiazolyl-2'-amino*)-6-*methoxyquinaldine*.—Prepared as above by using 2-amino-5-isopropylthiazole in the place of 2-aminothiazole in the above reaction. On crystallisation from alcohol, it separated in needles and had m.p. 226–8° (Found: N, 13·30. $C_{17}H_{19}ON_3S$ requires N, 13·4%).

4-(5'-*Ethylthiazolyl-2'-amino*)-6-*chloroquinaldine*.—Prepared from 4:6-dichloroquinaldine (5 g.) and 2-amino-5-ethylthiazole (3·05 g.) by heating them with phenol (25 g.). On crystallisation from benzene-ligroin, it had m.p. 169–70° (Found: N, 13·85. $C_{15}H_{14}N_3SCl$ requires N, 13·83%).

4-(5'-Iso*propylthiazolyl-2'-amino*)-6-*chloroquinaldine*.—Prepared from 4:6-dichloroquinaldine (5 g.), 2-amino-5-isopropylthiazole (3·4 g.) and phenol (25 g.). On crystallisation, it had m.p. 161–6° (Found: N, 13·18. $C_{16}H_{16}N_3SCl$ requires N, 13·23%).

4-(4'-*Methylpyrimidyl-2'-amino*)-7-*chloroquinoline*.—This compound was prepared by heating a mixture of 2-amino-4-methylpyrimidine (2·2 g.) 4:7-dichloroquinoline (3 g.) and phenol (20 g.) at 150° for 4 hours. The product crystallised from acetone in fine greenish yellow needles, m.p. 155° (Found: N, 20·45. $C_{14}H_{11}N_4Cl$ requires N, 20·70%).

Attempted condensation of 2-*amino*-4-*methyl*-6-*chloropyrimidine with* 4:7-*dichloroquinoline*.—The two compounds did not condense when they were refluxed in alcohol or pyridine or Dowtherm. When refluxed in amyl

alcohol, the compound obtained was identified to be 4-hydroxy-7-chloroquinoline, m.p. 272–3° (Found: N, 7·89. C_9H_6ONCl requires N, 7·77%). When the reactants were heated in phenol, 4-phenoxy-7-chloroquinoline hydrochloride, m.p. 203–5° and 2-amino-4-methyl-6-phenoxypyrimidine, m.p. 195–6° (Found: N, 20·20; 20·06. $C_{11}H_{11}ON_3$, $\frac{1}{2}$ H_2O requires N, 20·00) causing no depression with a sample prepared independently, were obtained.

4-*Phenoxy*-6-*chloroquinaldine*.—This was prepared from 4:6-dichloroquinaldine and phenol by heating them together. On crystallisation from acetone, it had m.p. 159–60° (Found: N, 5·27. $C_{16}H_{12}ONCl$ requires N, 5·19%).

4-*Amino*-7-*chloroquinoline*.—(i) A mixture of 4-phenoxy-7-chloroquinoline (1 g.) and ammonium acetate (5 g.) was heated at 170–75° for 3 hours. The reaction mixture was poured into water and rendered alkaline with aq. sodium hydroxide when a solid product separated. It was filtered and crystallised from hot benzene; m.p. 148–50° (yield, 0·45 g.).[4]

(ii) 4-Methoxy-7-chloroquinoline (1 g.) was mixed with ammonium acetate (5 g.) heated at 130–5° for 3 hours and the product worked up as usual. 4-Amino-7-chloroquinoline was obtained in a yield of 70%.

Summary

Ten thiazolylaminoquinolines of formula (I) have been prepared by heating the 4-chloroquinolines with 2-aminothiazoles in phenol medium, at about 150–60°. In some cases, instead of the compounds of formula (I), only the 4-phenoxyquinolines could be isolated. The 2-chlorolepidines do not undergo this condensation at all. 4:7-Dichloroquinoline condensed with 2-amino-4-methylpyrimidine to yield the compound (II); but 2-aminopyrimidine and 2-amino-4-methyl-6-chloropyrimidine did not react with the chloroquinoline. Evidence has been presented to show that in the condensation of the chloroquinolines with amines in phenol medium, the phenoxyquinoline is not the intermediate as was supposed by some authors. A different mechanism seems to operate.

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CHEMOTHERAPY OF MALARIA

VI. Quinolylsulphones

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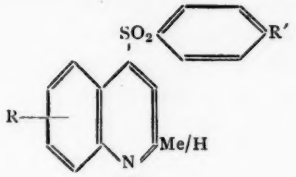
By heating 2-chloroquinoline with sodium arysulphinates, Troeger and Meinecke[1] synthesised the corresponding ary quinolyl sulphones. Surrey and Lindwall[2] prepared dipyridyl and diquinolyl sulphides and sulphones. Bambas[3] synthesised a series of 4-amino-phenylsulphones with a heterocyclic ring system attached to the sulphone group and of these the thiazole analog, "promizole" once received a great deal of attention. That derivatives of diamino-diphenylsulphone show antimalarial activity was shown by Coggeshall.[4] In view of the above, we synthesised phenylquinolylsulphones of general formula (I) with the hope that they may show antimalarial activity and also possess action against the exoerythrocytic forms of the plasmodia since many 4-hydroxyquinolines show this property.



(I)

The method of synthesis of the quinolylsulphones consisted of reacting 4-chloroquinoline derivatives with the substituted sulphinic acids which were used as sodium salts or in the presence of potassium acetate. In this work, 4:7-dichloroquinoline, 2-methyl-4:6-dichloroquinoline (4:6-dichloroquinaldine), 2-chloro-4-methyl-6-methoxyquinoline, 2-methyl-4-chloro-6-methoxyquinoline (4-chloro-6-methoxyquinaldine) and 2-chloro-4:6-dimethylquinoline were employed to condense them individually with the alkali metal salts of 4-acetaminobenzene sulphinic acid, 4-aminobenzenesulphinic acid, 4-acetaminomethylbenzenesulphinic acid, 4-chlorobenzenesulphinic acid and 2:5-dichlorobenzenesulphinic acid. The condensation of the 4-chloroquinolines with sulphinic acid salts proceeded with great ease when refluxed in ethanol solution; a small quantity of water was found to be essential for the reaction. The 2-chloroquinolines chosen for comparative study did not

condense under these conditions but the reaction proceeded at a higher temperature when heated in propylene glycol.

In the case of the dichloroquinolines that the 4-chlorine atom participates in the condensation has been shown by the fact that the sulphones obtained, on heating with acids, furnished the 4-hydroxy-quinolines. It has been found that the 4-quinoline sulphones readily undergo hydrolysis to the 4-hydroxy-quinolines.

The twenty-one compounds prepared have been presented in the table. They were tested for prophylactic antimalarial activity by feeding to mosquitoes infected with *Plasmodium gallinaceum* with negative results. Full details of these experiments will be reported elsewhere.

Experimental

The intermediate chloroquinolines were prepared by the standard methods of Knorr, Conrad and Lampach,[5] by the interaction of the requisite arylamines with ethylacetoacetate followed by cyclisation and the final conversion of the hydroxy to the chloroquinolines.

The sulphinic acids were prepared from the sulphochlorides by reduction with sodium sulphite.

4-(*p-Acetaminobenzenesulphonyl*)-7-*chloroquinoline* (*No.* 21).—4 : 7-Dichloroquinoline (5 g.), *p*-acetaminobenzenesulphinic acid (5 g.) and potassium acetate (2·5 g.) were refluxed in ethanol (100 c.c.) for 15–20 minutes. The reaction product that separated on cooling was filtered and washed with water (yield, 7·3 g., m.p. 222–24°). On crystallisation from ethanol it separated in long needles, m.p. 225°.

The above acetyl compound (5 g.) was refluxed with 12% hydrochloric acid (50 c.c.) for 15 to 20 minutes. From the solution a product m.p. 270° was isolated which was identified to be 4-hydroxy-7-chloroquinoline.

4-(*p-Aminobenzenesulphonyl*)-7-*chloroquinoline* (*No.* 22).—*p*-Aminobenzenesulphinic acid (5 g.) was taken up with potassium acetate (3 g.) and 4 : 7-dichloroquinoline (5 g.) in ethanol (150 c.c.), the mixture refluxed for about 2 hours and then kept aside. Next day, the solid that had separated was filtered, washed with water and dried (yield, 6·5 g. pale yellow needles, m.p. 233–35°). On recrystallisation from acetone, it had m.p. 233–6°. On acetylation, it furnished the acetamino compound described above (No. 21).

2-(*p-Acetaminobenzenesulphonyl*)-4-*methyl*-6-*methoxyquinoline* (*No.* 35).—2-Chloro-4-methyl-6-methoxyquinoline (4·15 g.) and potassium *p*-acetaminobenzenesulphinate (6 g.) were refluxed in a mixture of ethanol (30 c.c.) and

TABLE II

Sl. No.	Name of Compound	Formula	M. P.	Analysis	
				Found	Requires
					%
21	4-(*p*-Acetaminobenzenesulphonyl)-7-chloroquinoline	$C_{17}H_{13}O_3N_2ClS$	226° C.	Cl, 10·1 N, 7·7	9·8 7·8
22	4-(*p*-Aminobenzenesulphonyl)-7-chloroquinoline	$C_{15}H_{11}O_2N_2ClS$	235–36°	Cl, 11·4 N. 9·0	11·1 8·8
23	4-(*p*-Chlorobenzenesulphonyl)-7-chloroquinoline	$C_{15}H_9O_2NCl_2S$	147–48°	Cl, 21·1	21·0
24	4-(2′:5′-Dichlorobenzenesulphonyl)-7-chloroquinoline	$C_{15}H_8O_2NCl_3S$	158–59°	Cl, 28·4	28·6
25	4-(*p*-Acetaminomethylbenzenesulphonyl)-7-chloroquinoline	$C_{18}H_{15}O_3N_2ClS$	185–86°	Cl, 9·6	9·5
26	2-Methyl-4-(*p*-acetaminobenzenesulphonyl)-6 chloroquinoline	$C_{18}H_{15}O_3N_2ClS$	212°	Cl, 9·7	9·5
27	2-Methyl-4-(*p*-aminobenzenesulphonyl)-6-chloroquinoline	$C_{16}H_{13}O_2N_2ClS$	241–42°		
28	2-Methyl-4-(*p* chlorobenzenesulphonyl)-6-chloroquinoline	$C_{16}H_{11}O_2NClS$	192° d.	Cl, 20·1	20·1
29	2-Methyl-4-(2′:5′-dichlorobenzenesulphonyl)-6-chloroquinoline	$C_{16}H_{10}O_2NCl_3S$	165–66°	Cl, 28·0	27·6
30	2-Methyl-4-(*p*-acetaminomethylbenzenesulphonyl)-6-choroquinoline	$C_{19}H_{17}O_3N_2ClS$	213°	Cl, 8·9	9·15
31	2-Methyl-4-(*p*-acetaminobenzenesulphonyl)-6-methoxyquinoline	$C_{19}H_{18}O_4N_2S$	223–24°	N, 7·7	7·6
32	2-Methyl-4-(*p*-aminobenzenesulphonyl)-6-methoxyquinoline	$C_{17}H_{16}O_3N_2S$	237–38°	N, 8·4	8·5
33	2-Methyl-4-(*p*-chlorobenzenesulphonyl)-6-methoxyquinoline	$C_{17}H_{14}O_3NClS$	177–78°	Cl, 10·0	10·2
34	2-Methyl-4-(2′:5′-dichlorobenzenesulphonyl)-6 methoxyquinoline	$C_{17}H_{13}O_3NCl_2S$	183–84°	Cl, 18·9	18·6
35	2-(*p*-Acetaminobenzenesulphonyl)-4-methyl 6-methoxy-quinoline	$C_{19}H_{18}O_4N_2S$	259–60	N, 7·4	7·6
36	2-(*p*-Aminobenzenesulphonyl)-4-methyl-6-methoxyquinoline	$C_{17}H_{16}O_3N_2S$	221–22°	N, 8·6	8·5
37	2-(*p*-Chlorobenzenesulphonyl)-4-methyl-6-methoxyquinoline	$C_{17}H_{14}O_3NClS$	186–87°	Cl, 9·9	10·3
38	2-(*p*-Acetaminomethylbenzenesulphonyl)-4-methyl-6-methoxy-quinoline	$C_{20}H_{20}O_4N_2S$	264–65°	N, 7·2	7·3
39	2-(*p*-Acetaminobenzenesulphonyl)-4:6-dimethylquinoline	$C_{19}H_{18}O_3N_2S$	253–54°	N, 7·9	7·9
40	2-(*p*-Chlorobenzenesulphonyl)-4:6-dimethylquinoline	$C_{17}H_{14}O_2NClS$	177–78°	Cl, 10·8	10·7
41	2-(2′:5′-dichlorobenzenesulphonyl)-4:6-dimethylquinoline	$C_{17}H_{13}O_2NCl_2S$	196–98°	Cl, 19·6	19·4

water (10 c.c.) for 7 to 8 hours. The starting chloroquinoline was recovered back. On replacing ethanol by propyleneglycol and adding traces of copper bronze and iodine as catalysts the condensation product could be obtained (5·45 g. of white needles, m.p. 240–54°). On recrystallisation from a mixture ethanol and acetone, it had m.p. 259–60°.

On refluxing the above with 12% hydrochloric acid for about 30 minutes, the free amino derivative was obtained (No. 36), m.p. 221–2°.

Summary

Twenty-one aryquinolylsulphones described in the table have been prepared by reacting the chloroquinolines with substituted arylsulphinic acids. The 4-chloroquinolines furnish the sulphones very readily and these sulphones are easily hydrolysed to the corresponding 4-hydroxyquinolines.

These compounds do not show any activity when tested for their prophylactic activity in mosquitoes against *Plasmodium gallinaceum* infection.

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SYNTHETIC EXPERIMENTS IN THE BENZO-PYRONE SERIES

Part XVII. Some Isoflavono-7 : 8-Furans

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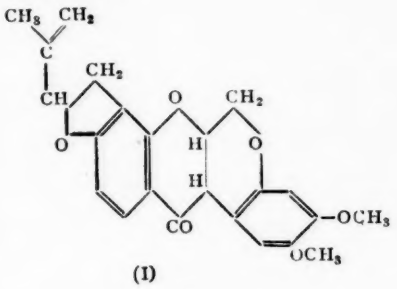
Rotenone (I) is one of the most powerful of the natural insecticides. It is a complex molecule containing five rings and it is not yet clear which parts of the molecule are intimately connected with its remarkable properties. According to Lauger and co-workers,[1] the group —CO—CH = CH—O— present in the chromanone part is a toxophore. But simpler molecules such as karanjin (II), 7-methoxy flavone (III) and flavanone (IV) and 7-methoxy-2-methyl-isoflavone (V) containing this group are considerably less efficient as fish poisons.[2]



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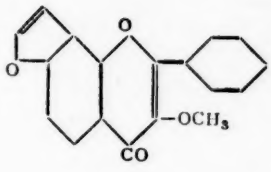

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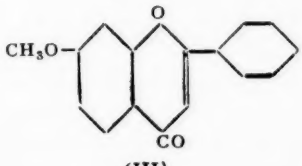

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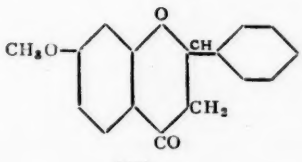

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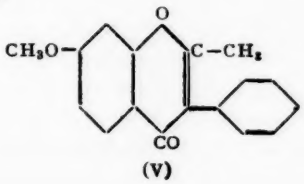
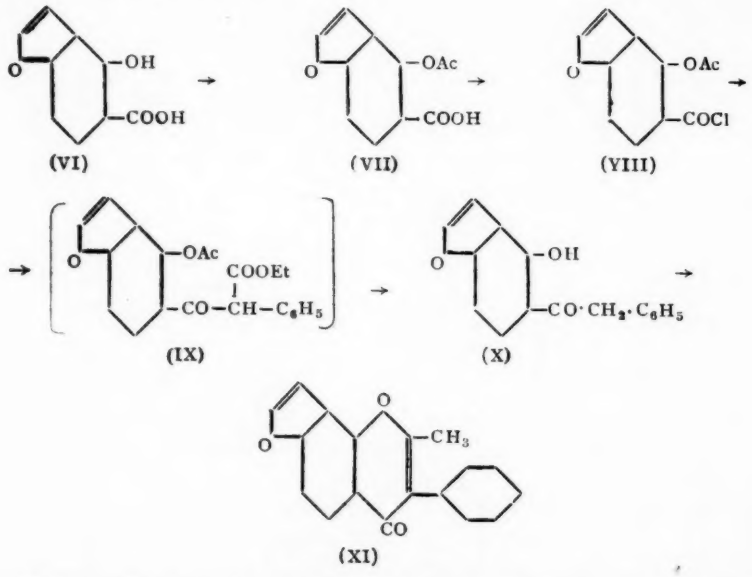


(V)

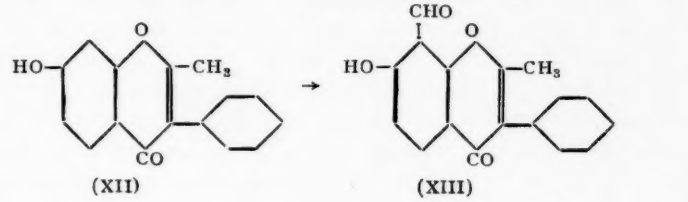
In attempts to gather more information on the effect of structure on toxic properties in the rotenone group, the synthesis of isoflavono-furans of the angular type has now been carried out. For this purpose two possible methods have been explored. The first starts with a suitable coumarone derivative and builds up the isoflavone structure on it; the second alternative begins with an isoflavone skeleton and builds up a furan ring on it. Both these methods have been previously employed in the synthesis of the flavono-furan, karanjin[3] (II).

For the first method karanjic acid (VI) which is fairly easily obtained as a product of hydrolysis of karanjin (II) is the starting material. Its synthesis has been worked out earlier by several groups of workers.[4] It is converted into its acetate (VII) and subsequently the acid chloride (VIII) and condensed with the sodium derivative of phenyl acetic ester. Subsequent hydrolysis and decarboxylation of the intermediate (IX) which is not isolated, yields benzyl-karanjyl-ketone (X). The isoflavone (XI) is obtained by boiling (X) with sodium acetate and acetic anhydride. A 2-methyl derivative is preferred since it is more closely related to rotenone than a compound unsubstituted in position 2.

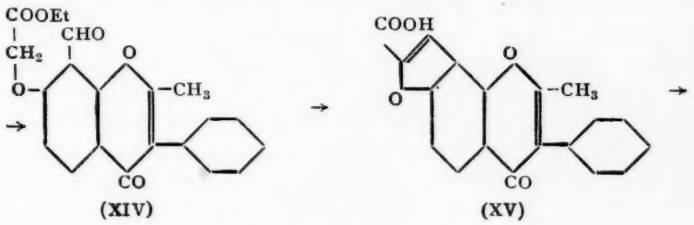


The second alternative method is found to give serious difficulties just as in the synthesis of karanjin (II). The starting material is 2-methyl-7-

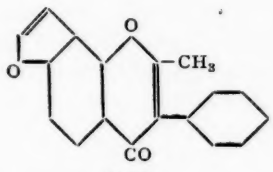
hydroxy-isoflavone (XII) which readily yields the corresponding 8-aldehyde (XIII) by the hexamine method. The next step involving condensation with bromacetic ester to yield the aldehydo-ester (XIV) also proceeds smoothly. Action of aqueous alkali, besides hydrolysing the ester, further brings about conversion into the furan-α-carboxylic acid (XV). This feature was first noticed in karanjin synthesis. The acid (XV) can be obtained more readily pure along with a small quantity of its own ester, by the action of alcoholic sodium ethoxide on the aldehydo ester (XIV). Final decarboxylation of the acid gives the corresponding furan (XVI) in poor yields only.



(XII) (XIII)



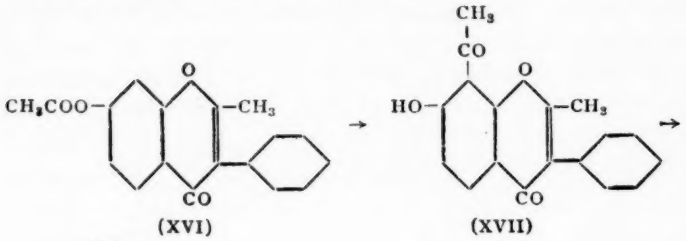
(XIV) (XV)



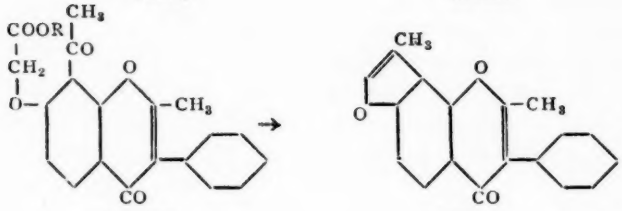
(XVI)

These difficulties are eliminated when a small modification in the synthesis is introduced. Instead of using 7-hydroxy-2-methyl isoflavone-8-aldehyde (XIII) the corresponding ketone (XVII) is made by the Fries migration of (XVI) and subjected to the series of reactions for building up the furan ring. Then every step proceeds smoothly, the carbethoxy-methyl ether (XVIII, R = Et) undergoes hydrolysis to give the corresponding ketonic acid (XVIII, R = H) and when this is boiled with sodium acetate and acetic anhydride ring closure and decarboxylation are effected and a good yield of 2: β-dimethyl-isoflavono-7: 8-furan (XIX) is obtained. Probable explanation of

this difference may be (1) the lower reactivity of a ketone group as compared with an aldehyde and (2) greater stability conferred on the furan structure by the presence of the β-methyl group.



(XVI) (XVII)



(XVIII) (XIX)

R=Et or H

Experimental

O-*Acetyl karanjic acid* (*VII*)

Karanjin required for this preparation was isolated from the oil of *Pongamia glabra* following the improved method of Rao, Rao and Seshadri.[5] Karanjic acid was obtained from it using the method of the same authors but it was not found necessary to keep an inert atmosphere in the reaction vessel. The presence of air did not affect the yields. For the preparation of the acetyl derivative of this acid the following modification of the original method[3] is found to be more convenient.

A solution of karanjic acid (1 g.) in anhydrous pyridine (3 c.c.) was cooled in ice-salt mixture and then treated with acetyl chloride (0·8 c.c.) drop by drop while stirring. After 30 minutes, the mixture was treated with crushed ice and dilute hydrochloric acid (10 c.c.). The acetyl derivative rapidly separated out as a colourless solid. It was filtered and crystallised from alcohol when it came out as colourless elongated prisms, m.p. 172–73°. Yield, 0·8 g.

4-*Hydroxy-coumarone-5-benzyl ketone* (*X*)

In an earlier paper[3] the acid chloride of acetyl karanjic acid was made using phosphorous pentachloride. This preparation has now been affected using thionyl chloride instead.

Well dried acetyl karanjic acid (1 g.) was treated with thionyl chloride (5 c.c.) and heated on a water-bath. In the course of a few minutes all the acid went into solution which was green coloured. The unreacted thionyl chloride was removed by distillation and the residue treated with carbon tetrachloride and filtered. The solvent was distilled off from the filtrate and the residual acid chloride was washed thrice with petroleum ether (5 c.c. each time). It was then obtained as a colourless viscous liquid which was directly employed for the next stage.

Freshly distilled ethyl phenyl acetate (1 c.c.) in anhydrous ether (25 c.c.) was treated with thin slices of metallic sodium (0·2 g.) and kept for 2 hours with occasional shaking. A profuse pale yellow precipitate of the sodium derivative appeared. It was fluffy and could with care be decanted along with ether into another flask thus separating it from the unreacted sodium metal. To this was added with stirring an ethereal solution of the acid chloride of acetyl karanjic acid. There was immediate reaction and the mixture became warm. After leaving overnight, it was gently refluxed for three hours and the ether was distilled off. The residue was next refluxed with 3% methyl alcoholic potash (30 c.c.) for two hours more. Alcohol was then removed under reduced pressure and water added. A dark brown solution was obtained. On acidification with hydrochloric acid, a pale yellow coloured solid separated out. It was filtered, agitated with 5% sodium bicarbonate solution to remove any karanjic acid that might have been formed and again filtered, washed with a little water and crystallised from alcohol when the coumarone ketone was obtained as rectangular plates melting at 105–6°. Yield, 0·4 g. (Found: C, 75·9; H, 5·0; $C_{16}H_{12}O_3$ requires C, 76·2 and H, 4·8%.) The ketone was easily soluble in alcohol, ether, benzene, acetone and ethyl acetate. It gave a violet blue colouration with alcoholic ferric chloride. It dissolved in aqueous alkali readily.

2-*Methyl-isoflavono*-7 : 8-*furan* (*XI*)

The coumarone-benzyl ketone (X) (0·5 g.) was refluxed with acetic anhydride (10 c.c.) and freshly fused sodium acetate (2 g.) for 12 hours. The excess of acetic anhydride was then decomposed by adding alcohol. Next day the mixture was distilled to remove alcohol and ethyl acetate and the residue taken up in ether. The ethereal extract was washed thrice with 5% aqueous sodium hydroxide and then with water. After drying over magnesium sulphate, ether was removed by evaporation. The residue quickly solidified on scratching with a glass rod. It was crystallised from alcohol when the isoflavono-furan (XI) was obtained as pale yellow stout prisms melting at 95–6°. Yield, 0·2 g. (Found: C, 78·1; H, 4·6; $C_{18}H_{12}O_3$ requires C,

78·3 and H, 4·3%.) It was easily soluble in alcohol, ether, acetone, benzene and ethyl acetate. It developed no colour with alcoholic ferric chloride. It did not go into solution in warm 5% aqueous alkali.

7-Hydroxy-8-formyl-2-methyl-isoflavone (*XIII*)

A mixture of 7-hydroxy-2-methyl-isoflavone[6] (2 g.), hexamine (8 g.) and glacial acetic acid (24 c.c.) was heated under anhydrous conditions on a vigorously boiling water-bath for six hours. The hot reddish brown liquid was then treated with 1 : 1 hydrochloric acid (24 c.c.) and heated again on the water-bath for about 5 minutes. After dilution with water (40 c.c.) it was allowed to remain overnight. There was a yellow precipitate which was collected, washed with water and dried in an air oven. The dry solid was extracted with hot benzene (25 c.c.) twice and the residue rejected. On concentrating the benzene extract, the hydroxy aldehyde (XIII) crystallised out as stout rectangular prisms melting at 164–5°. Yield, 1·0 g. It was easily soluble in aqueous alkali yielding a bright yellow solution. With ferric chloride a wine red colouration was obtained in alcoholic solution. (Found: C, 72·8; H, 4·4; $C_{17}H_{12}O_4$ requires C, 72·9 and H, 4·3%.)

7-Carbethoxy-methyl ether (*XIV*)

The above aldehyde (XIII) (2·8 g.) in anhydrous acetone (75 c.c.) solution was treated with ethyl bromo-acetate (1·2 c.c.) and anhydrous potassium carbonate (5 g.). After refluxing for six hours, the mixture was filtered and the filtrate distilled to recover acetone. The residue was treated with water and extracted thrice with ether. The ether extract was dried over anhydrous magnesium sulphate and the ether removed by distillation. The residue contained traces of ethyl bromo-acetate and was therefore washed thrice with small quantities of petroleum ether. It then solidified quickly when scratched with a glass rod. It was recrystallised twice from alcohol when the carbethoxy-methyl ether was obtained as colourless rectangular prismatic rods melting at 124–5°. Yield, 0·9 g. (Found: C, 68·6; H, 5·1; $C_{21}H_{18}O_6$ requires C, 68·9; H, 4·9%.)

The potassium salts residue left after filtering off the acetone solution, was dissolved in a little water and acidified with hydrochloric acid. A white solid precipitate (1·4 g.) was obtained which was found to be identical with 7-hydroxy-8-formyl-2-methyl isoflavone.

2-Methyl-isoflavono-7 : 8-furan-α-carboxylic acid (*XV*)

A suspension of carbethoxymethyl ether (XIV) (1 g.) in absolute alcohol (6 c.c.) was treated with sodium ethoxide (0·1 g. of sodium in 4 c.c. of alco-

hol). On stirring vigorously a yellow precipitate separated out. After 45 minutes the mixture was diluted with ether (50 c.c.), agitated and carefully decanted. Very little was present in the ether solution. The ether-insoluble solid residue dissolved in water (20 c.c.). On the addition of hydrochloric acid (2 c.c.) a bright yellow precipitate separated out. It did not crystallise well from ethyl or methyl alcohol, acetone or ethyl acetate. It was purified by dissolving in sodium carbonate (effervescence) and reprecipitating with hydrochloric acid. It melted at 253–5° (decomp.). Yield, 0·8 g. It gave no colour with ferric chloride in alcoholic solution. (Found: C, 70·9; H, 4·0; $C_{19}H_{12}O_5$ requires C, 71·3 and H, 3·8%.)

Esterification of acid (XV)

The carboxylic acid (0·5 g.) was dissolved in absolute alcohol (25 c.c.) and refluxed for eight hours after adding concentrated sulphuric acid (1 c.c.). When the solution was concentrated, the ester came out in the form of microcrystals melting at 225–7°. It was thus different from the original ester (XIV). (Found: C, 72·2; H, 4·8; $C_{21}H_{16}O_5$ requires C, 72·4; H, 4·6%.)

Decarboxylation of (XV) to 2-methyl isoflavono-7: 8-furan (XVI)

(*a*) Boiling the carboxylic acid (XV) with acetic anhydride and sodium acetate for two hours produced no appreciable change.

(*b*) The dry carboxylic acid (1·0 g.) was heated at 290–300° in a pyrex round-bottomed flask for 15 minutes. The cooled mass was broken up and warmed with 4% aqueous sodium hydroxide. The turbid dark reddish brown solution was repeatedly extracted with ether. The ethereal extract was washed with water and dried over calcium chloride and evaporated to dryness. A brown solid was left behind which was crystallised from acetone-petroleum ether mixture. The isoflavono-furan (XVI) separated out in the form of pale yellow stout prisms melting at 95–6°. Mixed m.p. with the sample prepared from karanjic acid was undepressed. Yield, 45 mg.

(*c*) A mixture of the dry carboxylic acid (0·5 g.) and copper bronze (0·5 g.) in absolute quinoline (25 c.c.) was refluxed for 45 minutes. It was cooled, diluted with ether (100 c.c.) and filtered. The filtrate was successively extracted with 1 : 1 hydrochloric acid (five times—25 c.c. each time), with 4% aqueous sodium hydroxide (thrice—20 c.c. each time) and finally with water. It was then dried over calcium chloride and evaporated to dryness. A pale yellow residue was obtained. It crystallised from acetone-petroleum ether as pale yellow prisms melting at 95–6°. Yield, 60 mg.

The isoflavono-furan dissolved in cold concentrated sulphuric acid to give a pale brownish yellow solution which on warming with a drop of ferric chloride solution turned dark brownish red.

The alkali washings from (*a*) or (*b*) on acidification gave rise to uncrystallisable products.

7-Hydroxy-8-acetyl-2-methyl-isoflavone (*XVII*)

An intimate mixture of 7-acetoxy-2-methyl-isoflavone[6] (XVI) (3·0 g.) and anhydrous aluminium chloride (5·5 g.) was heated at 170–80° in a conical flask protected from atmospheric moisture. At first, the contents melted into a dark coloured liquid but gradually solidified. After an hour and a half, it was cooled and treated with crushed ice and dilute hydrochloric acid (1 : 1, 75 c.c.). The dark solid slowly disintegrated when kept overnight. It was then heated on a wather-bath for 30 minutes and filtered hot. The solid residue was washed thoroughly with dilute hydrochloric acid and then with water. It was crystallised from alcohol twice when it was obtained as colourless star-like clusters of needles melting at 204–5°. Yield, 2·5 g. (Found: C, 73·2; H, 5·0; $C_{18}H_{14}O_4$ requires C, 73·5 and H, 4·7%.) It was soluble in alcohol, acetone and ether but only sparingly in benzene. It dissolved in dilute sodium hydroxide to give a pale yellow solution. With alcoholic ferric chloride, a brownish red colour was obtained. It dissolved in concentrated sulphuric acid to give brownish yellow solution with no fluorescence.

7-Carbethoxy-methyl ether (*XVIII*, $R = C_2H_5$)

A solution of (XVII) (2·0 g.) in dry acetone (120 c.c.) was treated with ethyl bromo-acetate (0·85 c.c.) and anhydrous potassium carbonate (5 g.) and refluxed for six hours. The inorganic salts were filtered off and washed with a little warm acetone. The filtrate was distilled to recover acetone and the residue taken up in ether. The ethereal extract was shaken twice with 2% aqueous alkali and then twice with water. After drying over anhydrous sodium sulphate, removal of ether gave a colouriess, viscous liquid, which solidified only after a few days. It crystallised from alcohol, as colourless prismatic crystals melting at 123-4°. Yield, 1·3 g. (Found: C, 69·2; H, 5·5; $C_{22}H_{20}O_6$ requires C, 69·5 and H, 5·4%.) It was easily soluble in alcohol, ether, acetone and benzene; but sparingly soluble in light petroleum. It did not dissolve in aqueous alkali and gave no colour with alcoholic ferric chloride.

7-Carboxy-methyl-ether (XVIII, R = H)

The above carbethoxy-methyl ether (1 g.) was treated with 3% aqueous potash (75 c.c.) and heated to 80° on a water-bath till all the solid went into solution (30 mts.). The resulting red solution was cooled and extracted with ether to remove any unhydrolysed material. On acidification, a colourless compound was obtained. It crystallised from acetone-petroleum ether mixture in the form of colourless prismatic crystals melting at 156–8°. Yield, 0·7 g. (Found: C, 68·0; H, 4·7; $C_{20}H_{16}O_6$ requires C, 68·2 and H, 4·5%.) It dissolved easily in sodium bicarbonate solution with effervescence and gave no colour with alcoholic ferric chloride.

β: 2-Dimethyl-isoflavono-7: 8-furan (XIX)

The above carboxylic acid (1·0 g.) was refluxed with freshly distilled acetic anhydride (15 c.c.) and fused sodium acetate (2 g.) for two hours. The excess of acetic anhydride was decomposed by pouring the cooled mixture into alcohol (45 c.c.). After leaving it overnight, the alcohol and the ethyl acetate were removed by distillation and the residue taken up in ether. The ethereal extract was thoroughly washed with 2% aqueous alkali to remove any unconverted carboxylic acid. It was dried over calcium chloride and distilled to remove ether. A colourless viscous liquid was obtained which did not crystallise even after three days. It was then taken up in acetone and petroleum ether added to turbidity. After some time the clear solution was carefully decanted and allowed to crystallise. Further crystallisation from alcohol yielded colourless needles melting at 170–1°. Yield, 0·4 g. (Found: C, 78·3; H, 5·1; $C_{19}H_{14}O_3$ requires C, 78·6 and H, 4·8%.) The substance was easily soluble in alcohol, ether and acetone. It was insoluble in aqueous alkali and developed no colour with ferric chloride.

Summary

Two methods of synthesising isoflavonofurans of the angular type are examined. Starting from karanjic acid (VI) and passing through the intermediate (X), 2-methyl-isoflavono-7: 8-furan (XI) is easily obtained. The alternative method which starts with 2-methyl-7-hydroxy-isoflavone (XII) and builds up the furan ring through the 8-aldehyde (XIII) is beset with difficulties. However if instead of the aldehyde, the corresponding ketone (8-acetyl derivative XVII) is employed the difficulties are eliminated and good yield of 2: β-dimethyl-isoflavono-7: 8-furan (XIX) is secured.

Our thanks are due to the Imperial Chemical Industries, Ltd., and the National Institute of Sciences of India for the award of a Fellowship to one of us (L. R. R.).

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BROMINATION OF COMPOUNDS CONTAINING TWO AROMATIC NUCLEI

Part IX. Bromination of Aryl Esters of 3-Nitro Salicylic Acid

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(Communicated by Dr. Mata Prasad, F.A.SC.)

This work was undertaken with a view to study towards bromination the effect of a negative group like $-NO_2$ in the acidic part of aryl esters of salicylic acid. It has been observed in the case of aryl esters of 3-nitro salicylic acid that bromine enters the acid part only when bromination is carried out in presence of a solvent like acetic acid and no bromine enters the phenolic part even when excess of bromine is used.

On the other hand bromination with liquid bromine always gives compounds with bromine in the phenolic part only. Phenyl ester gives a dibromo derivative whilst *o,m,*-cresyl esters give mono bromo derivatives only, even with a large excess of bromine. This points out that the course of bromination is controlled by the conditions of the reaction and not by the total quantity of bromine.

The constitutions of these bromo derivatives are proved by alkaline hydrolysis and confirmed by their synthesis.

Experimental

Bromination in acetic acid medium: *Phenyl 5-bromo-3-nitro-salicylate.*—Phenyl 3-nitrosalicylate (3 g.) was dissolved in acetic acid (10 c.c.) and solution of 2 g. of bromine in 5 c.c. acetic acid was added to it. The mixture was heated on a boiling water-bath for four hours. Solid that separated on cooling the solution was crystallised from carbon tetrachloride, m.p. 123–24°. Found: Br, 23·9; $C_{13}H_8O_5NBr$ requires Br, 23·7 per cent.

o-Cresyl 5-bromo-3-nitrosalicylate.—This was prepared in the same way as the phenyl ester. It crystallised from methyl alcohol, m.p. 138–39°. Found: Br, 22·8; $C_{14}H_{10}O_5NBr$ requires Br, 22·7 per cent.

m-Cresyl 5-bromo-3-nitrosalicylate was prepared in the same way as the ortho isomer. It crystallised from ethyl alcohol, m.p. 131–32°. Found: Br, 22·9; $C_{14}H_{10}O_5NBr$ requires Br, 22·7 per cent.

Bromination with liquid bromine

2:4-*Dibromophenyl* 3-*nitrosalicylate*.—Liquid oromine (6 g.) was gradually added to phenyl 3-nitrosalicylate (4 g.) and the mixture ws shaken for half an hour and then left overnight. The mixture was diluted with water and then treated with dilute solution of sodium bisulphite and the solid obtained crystallised from ethyl alcohol, m.p. 157–58°. Found: Br, 38·5; $C_{13}H_7O_5NBr_2$ requires Br, 38·4 per cent.

4-*Bromo-o-cresyl*-3-*nitro-salicylate*, m.p. 123–24°, and 4-*bromo-m-cresyl* 3-*nitro-salicylate*, m.p. 131–32°, were prepared in the same way as the phenyl derivative by using 4 g. of ester and 3 g. of liquid bromine. Both crystallised from alcohol. The former gave Br, 22·8 and the latter gave Br, 22·9 whilst $C_{14}H_{10}O_5NBr$ requires Br, 22·7 per cent.

Hydrolysis

All bromo derivatives described above were hydrolysed by boiling (1 g.) of the substance with 100 c.c. of 5 per cent. sodium hydroxide solution for about five to six hours. The solution was cooled in ice and carbon dioxide was passed through it when the phenolic component separated. It was removed by extraction with ether. The residual aqueous solution was then acidified and the acid obtained was crystallised and identified by mixed melting point.

Synthesis

The esters of 5-bromo-3-nitrosalicylic acid were also prepared by condensing the acid (2 g.) with the appropriate phenol (2 g.) in presence of phosphorus oxychloride (1 c.c.) by heating the mixture at 120–30° for about half an hour. Their mixed melting points with the bromination products showed no lowering.

Melting point of the bromo aryl esters of 3-nitro-salicylic acid showed no lowering, when mixed with the synthetic products described by Jadhav and Thakkar[1].

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INVARIANTS OF A TENSOR OF RANK 2

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Introduction

It is well known[1] that, given a vector A^k in a space whose metric properties are defined by the symmetric tensor g_{kl} (the "fundamental tensor"), we can use the g_{kl} to define a vector A_k with a lower index:

$$A_k \equiv A^l g_{lk} \qquad \text{(summation convention assumed)}$$

which transforms contragradiently to A^k; and then all the rational integral invariants that can be formed from A^k are expressible as polynomials in

$$A^2 \equiv A^k A_k.$$

The question arises as to whether in the next simplest case of a tensor of rank 2 the possible invariants can be expressed in terms of a finite basis and of finding the basis. It can be shown[2] that any invariant which is rational integral in the components of such a tensor F^{kl} can be expressed as a polynomial in the invariants $I_1, I_2, \ldots I_m, \ldots$, where

$$\begin{aligned} I_1 &= F_k^k \\ I_2 &= F^{kl}F_{lk} \\ &\cdots\cdots\cdots\cdots \\ I_m &= F^{kl}F_{lr}F^{rs}\ldots F_{.k} \qquad (1) \\ &\cdots\cdots\cdots\cdots \end{aligned}$$

It is the purpose of this note to establish the existence of a finite basis for these invariants.

§ 1. *Lemma.*—The traces of the matrix-powers $\mathbf{F}, \mathbf{F}^2, \ldots \mathbf{F}^m, \ldots$ are expressible as rational integral functions of the traces of the first n of them, n being the number of rows or columns of the matrix.

This follows from the fact that

$$T_r(\mathbf{F}) = \sum_{r=1}^{n} \lambda_r^m,$$

[1] *cf.* for example H. Weyl, *Classical Groups.*

[2] *cf.* for example H. J. Bhabha, *The Theory of Elementary Particles*, Part I, Chap. 5.

where λ_r are the eigenvalues of the matrix.

Also, $$T_r(F^m) = \sum_{r=1}^{n} \lambda_r^m,$$

since the eigenvalues of F^m are λ_r^m. The traces thus are the forms

$$\sum_{1}^{n} \lambda_r$$

$$\sum_{1}^{n} \lambda_r^2$$

$$\ldots\ldots$$

$$\sum_{1}^{n} \lambda_r^m$$

$$\ldots\ldots$$

Now it is well known that the first n of these form a rational integral basis for symmetric functions, and hence, in particular, it follows that all the traces are expressible in terms of the first n.

§ 2. *Theorem.*—The number of independent rational integral invariants which can be constructed from a tensor of rank 2 in a space of n dimensions is at most n. For an anti-symmetric tensor it is $n/2$ or $(n-1)/2$ according as n is even or odd.

We can write the mth invariant (1) as

$$I_m = F^k{}_l F^l{}_r F^r{}_s \ldots\ldots F^p{}_k$$
$$= T_r(F^m)$$

and then by the above lemma all the invariants are expressible as polynomials in the first n.

In the case of a skew-symmetric tensor, the odd-invariants, *i.e.*, those formed as a contracted product of an odd number of Fs, vanish in virtue of the anti-symmetry. We are, therefore, left with only $n/2$ or $(n-1)/2$ invariants in the basis, according as n is even or odd.

It may be remarked that all the rational integral invariants of a tensor of rank 2 thus formed are symmetric functions in the eigen-values of the matrix F. Conversely, all symmetric functions in these eigen-values are rational integral invariants of the tensor.

I wish to thank Professor Bhabha for suggesting the problem.

ON THE SCATTERING OF MESONS IN A 2 CM. LEAD PLATE

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Introduction

Experiments on the scattering of mesons by plates of copper, lead, gold and tungsten, have been performed by various workers. Wilson (1940) and Code (1941) using a Wilson cloud chamber with a magnetic field have been able to confirm the Gaussian distribution of the number of particles as a function of the product of the energy E and the scattering angle θ as expected from Williams' (1939) theory. They were also able to confirm within the experimental errors the theoretical mean value of $E \times \theta$ as expected from Williams' (1939) formule. The magnetic field used on the chamber gave these workers the advantage of knowing fairly accurately the energy of the scattered particle. In their experiments the energy of the particles was in the range 2×10^8 e.v. to 2×10^9 e.v. However the magnetic field also has the disadvantage of setting a bias against the large angle scatterings, by bending the particles scattered through large angles out of the range of the lower counters, or throwing them out of the illuminated region of the chamber. It also sets a bias against the low energy particles by bending them out of the counter geometry.

Shutt (1942) and recently Sinha (1945) have measured the scattering angles of particles in lead plates inside a Wilson chamber without a magnetic field. Shutt (1942) has measured a very large number of particles in 1 and 5 cm. of lead with a 16 cm. lead block above the chamber. He has assumed Williams' (1939) formulæ and has calculated by an original method the average nuclear scattering cross-section of the mesons. His value seems to agree fairly well with the average value of Marshak and Weisskopf (1941) assuming Hartree's energy distribution. Sinha (1945) working with an experimental arrangement of Geiger counters in coincidence and anti-coincidence was able to select particles within certain energy limits. He worked with two groups of energies, ranging from $0{\cdot}55 \times 10^8$ e.v. to $1{\cdot}5 \times 10^8$ e.v. and $1{\cdot}8 \times 10^8$ e.v. to $2{\cdot}5 \times 10^8$ e.v. Using two thicknesses of lead plates, namely, 2 cm. and 4 cm., he has made an attempt to calculate

the average nuclear scattering cross-section of the mesons. His value seems to agree well with the theoretical values calculated by Bhabha (1941), Weinberg (1941), and Ma and Hsuh (1944) in the energy region investigated by him.

The above mentioned theoretical workers show in their calculations a maximum of the nucleur scattering cross-section for a certain energy and a falling off on either side.

In the following experiment an attempt was made to check qualitatively the above calculated maximum. In order to differentiate between Coulomb scattering and nuclear scattering, we have assumed William's (1939) scattering formulæ for Coulomb scattering, and have made use of his result, that for cosmic-ray particles a fairly sharp separation in angular range is to be expected between scattering in the Coulomb field of the scattering atom and that arising from the short range interactions. Measurements of scattering therefore offer a method of estimating the magnitude of the short range interaction of mesons and nucleons.

Experimental

The experimental arrangement used is shown in Fig. 1.

The counters C_1, C_2 and C_3 are in triple coincidence. C_3 is a tray of three counters in parallel. The distances between these counters were kept the same throughout the experiment. Counters C_1 and C_2 were 15 cm. by 3·5 cm. and counters in the tray C_3 were each 30 cm. by 3·5 cm. A 2 cm. thick lead scattering block was kept inside the chamber. Four different thicknesses of lead, namely, 5, 15, 25 and 35 cm., were introduced between the counters C_2 and C_3. Approximately 280 photographs were taken for each thickness of these lead blocks. With this arrangement we were able to select particles of ranges R greater than 5, 15, 25 and 35 cm. of lead. Throughout the experiment no lead was kept above the chamber.

To get a measure of the distortion of the tracks in the chamber a hollow wooden box of dimensions and shape identical to those of the 2 cm. lead plate, was kept inside the chamber. In this particular case a 2 cm. lead block was kept above the chamber to cut out the slow electrons. About 42 photographs of tracks coming out singly from the top lead block and passing through the wooden box were selected, and their scattered angles measured. No cases of scatter greater than 2° were observed. Out of the above 42 tracks, 34 lay in the interval (0–1°) and 8, in the interval (1–2°).

A Blackett (1934) type of Wilson cloud chamber was used with slight modifications. A latex rubber diaphragm was stretched across the chamber

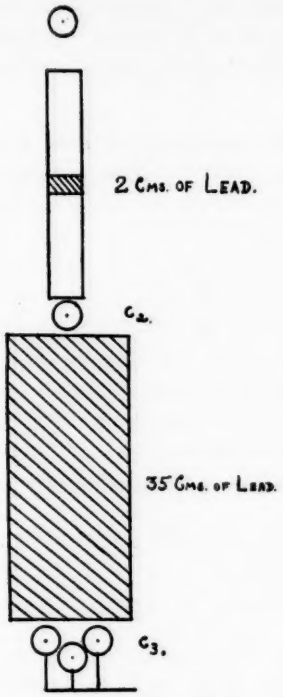

Fig. 1. Experimental Arrangement

between two perforated metal plates. The original metal piston drilled with holes was used as the back plate. Its forward and backward movement, controlled by the three back screws, served to change the expansion ratio. An aluminium plate drilled similarly with holes served as the front plate. The expansion mechanism was the same as that of Blackett's. The expansion chamber was 28 cm. in diameter and 10 cm. deep. The usual ethyl alcohol-water mixture in the ratio 70 : 30 with a mixture of argon and oxygen was used. The pressure of the gas in the chamber before expansion was 1·3 atmospheres. The clearing field was 100 volts.

Illumination was provided by six tungsten filament lamps, each rated at 110 votls 200 watts flashed for approximately a quarter of a second at 230 volts. Spherical condenser lenses were used to condense the light of these lamps on the chamber. The illuminated region was about 4 cm. deep. Stereoscopic photographs were taken by two F 2·8: I, $f = 5$ cm. Tessar

lenses, on Kodak 35 mm. Super XX film. The cameras made an angle of $22\frac{1}{2}$ on either side of the perpendicular to the plane of the chamber.

The scattering angles were measured with the mirror, and lamp and scale arrangement; the mirror being attached to the goniometer eye-piece of the microscope. Since all the tracks had to be grouped within one degree intervals of angles, with a majority of tracks no great accuracy was aimed at. This saved a lot of time on the measurements as more than 2,000 tracks had to be measured. But with a few tracks which were on the borderline, *i.e.*, where there was a doubt as to whether it could be grouped in the interval (0–1°) or in (1°–2°), several independent readings were taken for the same track and here the accuracy of measurement was within 6′.

For measurements 250 tracks which passed through the 2 cm. lead plate singly, without multiplication, and un-accompanied by other tracks, were selected from each of the ranges **R**. This selection helped to exclude the electrons. Protons however could not be excluded except at energies lower than the energy where they start ionising at least two or three times the minimum.

Results

The results tabulated in Table I, give measurements for the four different ranges of R (namely, $R > 5$ cm., > 15 cm., > 25 cm. and > 35 cm.

TABLE I. *The angular distribution of the particles for the four ranges of R, for both the cameras*

θ	N Number of particles (Total 250 in each range of R)											
Angular range	Left hand camera				Right hand camera				Average of the two Camera groups			
	R>5 cm.	R>15 cm.	R>25 cm.	R>35 cm.	R>5 cm.	R>15 cm.	R>25 cm.	R>35 cm.	R>5 cm.	R>15 cm.	R>25 cm.	R>35 cm.
0–1°	202	208	215	210	195	201	219	199	198·5	204·5	217	204·5
1°–2°	4	4	11	21	8	7	12	30	6	5·5	11·5	25·5
2°–3°	15	12	9	14	15	13	11	7	15	12·5	10	10·5
3°–4°	12	8	7	1	11	15	2	8	11·5	11·5	4·5	4·5
4°–5°	4	4	5	0	9	3	2	0	6·5	3·5	3·5	0
5°–6°	4	0	1	0	3	1	0	1	3·5	0·5	0·5	0·5
6°–7°	0	2	0	1	1	3	0	2	0·5	2·5	0	1·5
7°–8°	5	3	0	1	1	2	1	0	3	2·5	0·5	0·5
8°–9°	1	3	0	1	1	1	1	1	1	2	0·5	1
9°–10°	2	0	0	0	3	1	0	1	2·5	0·5	0	0·5
10°–11°	0	1	0	0	1	0	0	1	0·5	0·5	0	0·5
11°–12°	0	1	0	1	1	0	0	0	0·5	0·5	0	0·5
>12°	1	2	2	0	1	2	2	0	1	2	2	0

of lead) for each of the two cameras and the average of the two camera groups. Results of each of the two stereoscopic cameras have been recorded separately, instead of the usual average of the two stereoscopic angles, as the cameras were at an angle of 45° to each other, and a large angle in one of them would in a majority of cases be recorded as a very small angle in the other.

In the above table, column one gives the angular ranges, columns two to five give the number of particles for the different ranges of R, for the left hand camera, and are plotted in the form of block diagrams in Fig. 2. Columns six to nine give the same as above for the right hand camera, and have been plotted in Fig. 3. Columns ten to thirteen are the averages of the columns two to six, three to seven, etc., and have been plotted for two ranges of R in Fig. 5.

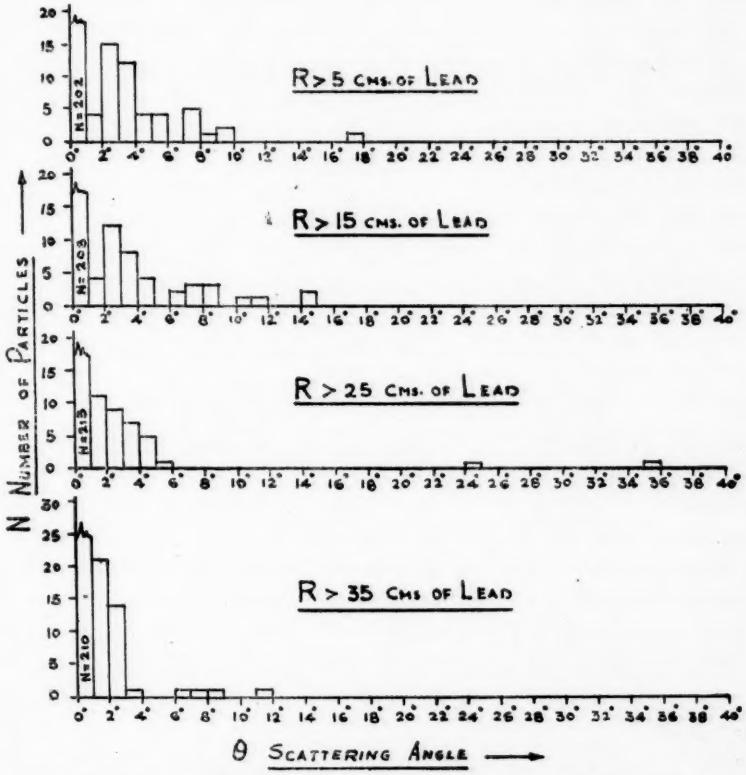

FIG. 2. The angular ranges against the number of particles N for the different ranges of R; for the left hand camera

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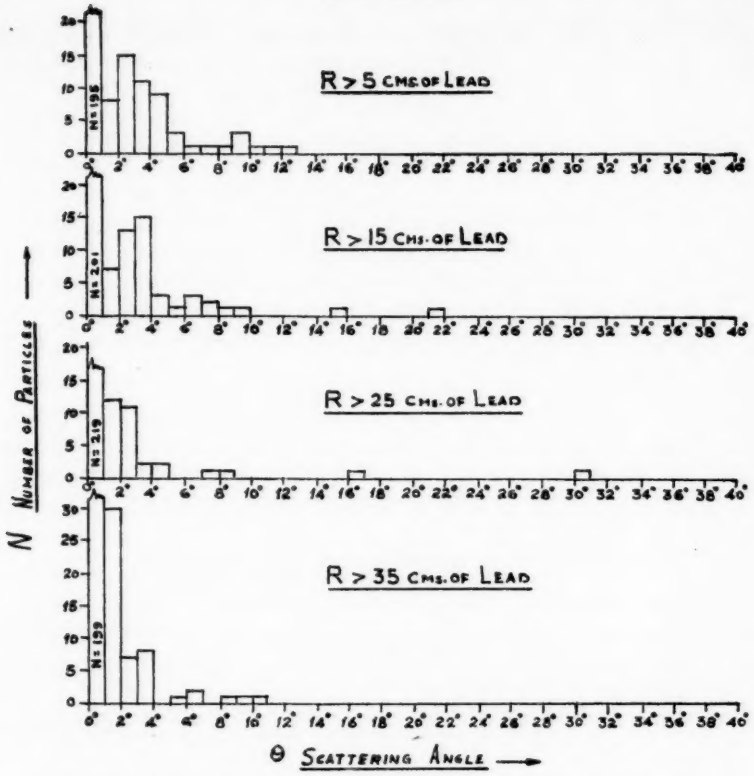

FIG. 3. The angular ranges against the number of particles N for the different ranges of R ; for the right hand camera

From Figs. 2 and 3, it is obvious that as the lower energies are being cut off by the various thicknesses of lead, the Coulomb scattering distribution between 1° and 6° shifts systematically towards the smaller angles. In the same figures, in the diagrams for $R > 5$ cm. and $R > 15$ cm. of lead there is an indication of a decrease in the angular range (1°–2°), which is not observed in the lowest diagram of $R - 35$ cm.

The Coulomb scattering as will be shown in detail later ends at about 12° and so thanks to the sharp cut-off of the tail of single scattering, all the scattering angles beyond this angle are assumed to be due to short-range nuclear forces.

Table 2 gives the number of large angle scatterings for each range of R. From this table one would be justified in saying that there is no maximum of the nuclear scattering cross-section at a certain energy, although

of course the number of large angle scatterings observed for each range R is very small.

TABLE II. *Number of large angle scatterings for the various ranges of R*

Range, R	R > 5 cm.	R > 15 cm.	R > 25 cm.	R > 35 cm.
No. of particles with $\theta > 12°$ ..	1	2	2	0

THEORETICAL

The detailed general treatment of this problem is due to Williams (1939), and only the main features of the results which are applicable to our experiment are given here.

The scattering is considered in terms of an effective impact parameter and two separate cases are distinguished according as the impact parameter is greater or less than a value r_0 which is approximately the nuclear radius. The main observed scattering arises from a range of impact parameters greater than r_0. This is effectively scattering in the Coulomb field of the nucleus, between extreme collision distances, the upper limit being determined by the shielding of the orbital electrons, and the lower limit (r_0) by the modification of the electrostatic field within the nucleur radius. These Coulomb collisions would normally lead to an angular distribution mainly due to multiple scattering, together with a tail of large angle single scattering, corresponding to close collisions. Williams (1939) shows that the effect of the lower limiting impact parameter is to suppress completely this tail of single scattering and to modify slightly the magnitude, but not the form, of the multiple scattering distribution. Hence the scattering due to these more distant collisions is entirely multiple and the distribution of observed scattering angles should be strictly Gaussian.

We may consider the closer collisions which correspond to a distance of approach less than (r_0) in terms of scattering due to the constitutent nuclear particles. It is shown by Williams (1939) that for these collisions the scattering in the Coulomb field of separate nuclear protons is negligible, and that any scattering distribution from this region is due to the short range interaction between the scattered particle and the individual neutrons and protons in the nucleus. The short range forces produce relatively many more large angle deflections than arise from the multiple Coulomb scattering. The predicted absence of a single scattering tail to the Gaussian of

electrical scattering is thus particularly favourable to the detection of scattering due to close collisions with nuclear particles.

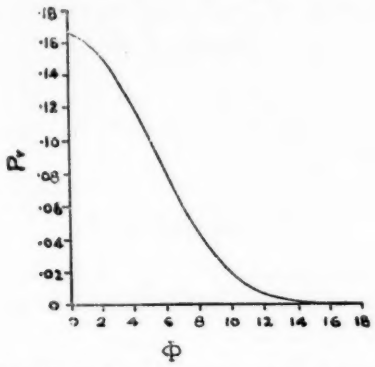

FIG. 4. Theoretical distribution of scattering [Taken from Williams (1939)]

The resultant scattering distribution of the multiple and single Coulomb scatterings is given in Fig. 4, which is taken from Williams' (1939) paper. The abscissa ϕ give the scattering angles in units of $\delta = \frac{600\,Ze\sqrt{(Nt)}}{\beta E}$ for a scattering material of atomic number Z, thickness t, and N atoms per cm.^{3}, and for a scattered particle of single charge, of energy E, and of velocity $v = \beta c$. Thus for every energy E, there is a separate angular distribution, with the abscissa given by $\theta° = \phi\delta$.

Since the energies of the particles are unknown, we have assumed Wilson's (1946) energy spectrum measurements at London and have made an attempt to calculate the theoretical distributions of angles for this spectrum. In Fig. 5, we have compared our experimental distributions for two ranges of R, namely $R > 5$ cm. and $R > 35$ cm., with the theoretical distributions calculated with the help of Fig. 4, and the above mentioned energy spectrum.

The theoretical distributions were calculated in the following way. The above mentioned Wilson's (1946) energy spectrum was first reduced to our total number of 250 particles for each range R. Then from this reduced spectrum the number of particles (n) for each energy interval of $0{\cdot}5 \times 10^9$ e.v. was selected. The mean energy E, lying in this interval was used to plot the distribution of Fig. 4, for this total of (n) particles. The sum of these distributions for all these intervals of energy is the resultant distribution given in Fig. 5.

Tables 3 and 4 give the individual distributions of Fig. 4 for each energy interval; for ranges of $R > 5$ cm., $R > 35$ cm. respectively. The

TABLE III. *The individual distributions of Fig. 4, for each energy interval, for $R > 5$ cm.*

$R > 5$ cm. of lead

Angular range	Number of particles (m) for each energy interval (in units of 10^9 e.v.)					Sum of the individual distributions
θ	0–0·5	0·5–1	1–1·5	1·5–2	>2	N
0–1° ..	6	11	38	31	97	183
1°–2° ..	5	10	17	5		37
2°–3° ..	4	8	4			16
3°–4° ..	2	5				7
4° 5° ..	1	2				3
5°–6° ..	1	2				3
6°–7° ..	0	1				1
(n) from Wilson's spectrum	19	39	59	36	97	

TABLE IV. *The individual distributions of Fig. 4, for each energy interval, for $R > 35$ cm. of lead*

$R > 35$ cms of lead

Angular range	No. of particles (m) for each energy interval (in units of 10^9 e.v.)				Sum of the individual distributions
θ	0·5–1	1–1·5	1·5–2	> 2	N
0–1° ..	12	42	34	104	192
1°–2° ..	11	19	5		35
2°–3° ..	8	4			12
3°–4° ..	5				5
4°–5° ..	3				3
5°–6° ..	2				2
6°–7° ..	1				1
(n) from Wilson's spectrum	42	65	39	104	

ratios of the areas below the curve of Fig. 4 are taken, for arriving at the number of particles (m) in each angle interval for a total number of (n) particles selected from the energy spectrum. Columns 2 to 6 give the individual distributions for each energy interval for a total number of (n) particles in that interval, and column 7 gives the sum of these individual distributions as they are plotted in Fig. 5.

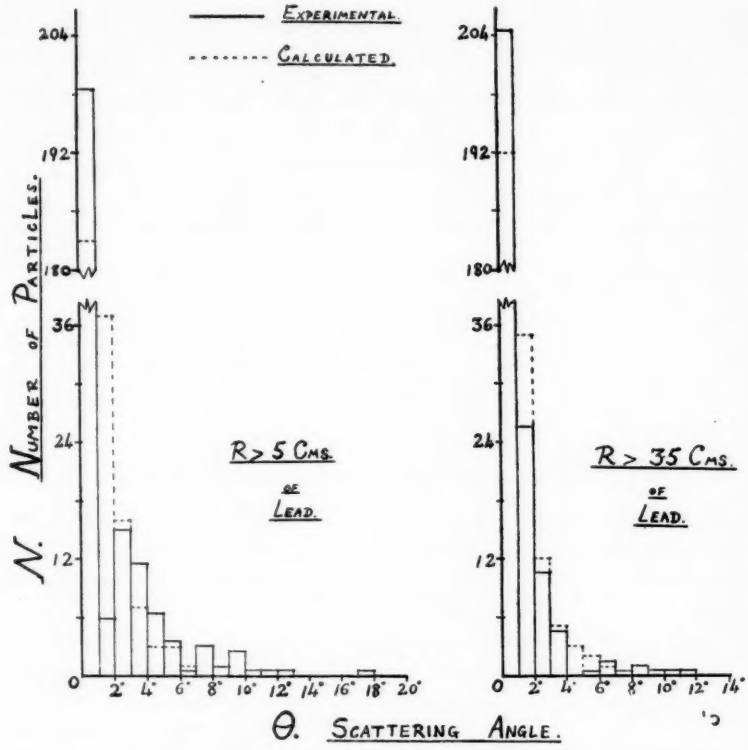

FIG. 5. A comparison of experimental and calculated distributions for two ranges of R ($R > 5$ cm. and $R > 35$ cm.)

DISCUSSION

In Fig. 5, we observe that the theoretical distributions calculated from the assumed Wilson's (1946) spectrum seem to be in fairly good agreement with the experimental distributions, for the degree interval (0–1°) where most of the particles are concentrated and where the number of particles is sufficiently large to justify a comparison with theory. The group of particles in the angular range (1°–2°) is abnormally low for the range $R > 5$ cm. being well below the theoretical value. Even for the range $R > 35$ cm., the value for this angular interval is outside the standard deviation. We have not been able to explain this descrepancy. The rest of the groups may be considered in fairly good agreement with the calculated groups, considering the fact that the number of particles in these groups is very small, with the consequent large statistical fluctuations.

The experimental distributions are continuous upto about 12 degrees, and since the theoretical distributions end at about 7 degrees, and remembering the sharp cut off of the tail of electrical distributions, we are justified in assuming that all angles beyond 12 degrees are due to nuclear scattering. As Williams (1939) points out, for a particular energy, the actual probability of scattering beyond this sharp cut.off for electrical interactions alone is about 0·0001. Since the energy spectrum at a lower latitude like Bombay is expected to be harder than at London; with a smaller percentage of low energy particles; we may safely say that the angle of 12 degrees is the upper limit.

From Table II, we have five cases of large angle scatterings for a traversal of 2000 cm. of lead; thus giving the range in lead for scattering, due to short range forces, of the order of 400 cm. This gives a lower limit for the cross-section of the order of 4×10^{-28} cm.^{2} per nucleon. This value is in fairly good agreement with the values obtained by other experimental workers. Wilson (1940) gives a value of 4×10^{-28} cm.^{2} per nucleon, Code's (1941) value as calculated by Shutt is $5{\cdot}7 \times 10^{-28} \pm 35\%$ cm.^{2} per nucleon. Shutt's (1946) value is from 2×10^{-28} to $4 \times 10^{-28} \pm 20\%$ cm.^{2} per nucleon for the angular range (9°–27°) for all energies of the energy spectrum. Sinha (1945) however gets a cross-section of the order of $2 \times 10^{-26} \pm 25\%$ cm.^{2} per nucleon for energies from $0{\cdot}5 \times 10^8$ to $2{\cdot}3 \times 10^8$ e.v. This higher value could be explained if the cross-section increases rapidly with lower energies. Amaldi and Fidecaro (1951) very recently working with counters have obtained a cross-section of the order of 10^{-29} cm.^{2} per nucleon.

The experimental values of Wilson chamber workers, mentioned above, are of the same order of magnitude as the theoretical values of various theoretical workers. According to Shutt (1942), if we average the theoretical expression for σ as a function of E, given by Marshak and Weisskopf (1941), over Hartree's energy distribution, we get the resultant theoretical average cross-section per nucleon, $\sigma = 3{\cdot}8 \times 10^{-28}$ cm.^{2} This value is in very good agreement with the experimental values quoted above. Bhabha (1939) calculates the value of the order of 10^{-27}—10^{-28} cm.^{2} per nucleon. Heitler and Peng's (1942) value is of the order of 2×10^{-27} cm.^{2} per necleon. Ma and Hsuh's (1944) and Weinberg's (1941) values are of the order of 10^{-26} cm.^{2} per nucleon.

However in this discussion so far we have assumed that we are dealing with mesons, but, we cannot exclude the possibility of other particles, like π-mesons, electrons from low density air showers and protons, contributing to these large angle scatterings.

The effect due to π-mesons may be neglected as the π-meson component is an extremely small percentage of the total component.

Calculations from the air shower theory (Broadbent and Janossy, 1948) gives us 0·1 of an electron as the number which would go through the 2 cm. lead plate inside the chamber without multiplication and unaccompanied by any other particle in the chamber, in the total sensitive time of our experiment. Thus the contribution due to electrons is very small.

Mylroi and Wilson (1951) give a proton component of 1% of the total hard component. However for our ranges of $R > 15$ cm. and $R > 25$ cm. we have cut out protons of momenta less than $0{\cdot}93 \times 10^9$ e.v./c. and $1{\cdot}17 \times 10^9$ e.v./c. respectively (*Princeton Range Tables*, E. P. Gross, 1947). And so from the above mentioned proton spectrum we get a proton component of 0·6% of the total hard component, for momenta greater than 10^9 e.v./c. Taking the above mentioned two ranges together we have thus three protons for a total of 500 particles; since each range has a total of 250 particles. Assuming a cross-section of 10^{-26} cm.^{2} per nucleon for proton-nucleon interaction (equivalent to an interaction range of 14 cm. of lead) we have of the above three protons only 0·4 of a proton scattered through a large angle. Against this we have from Table II, four large angle scatterings for these 500 traversals. This is ten times the contribution due to protons and thus cannot be all explained by protons.

Taking into consideration these corrections due to protons and electrons we get the lower limit of the cross-section for the meson—nucleon interaction of the order of 2 to 3×10^{-28} cm.^{2} per nucleon.

I wish to express my grateful thanks to Prof. H. J. Bhabha, F.R.S., for suggesting the problem and for helpful guidence and keen interest throughout the work. I am also very much indebted to Dr. J. G. Wilson, for very helpful discussions. I must also thank Mr. G. H. Vaze, who measured all the angles and Mr. Hardiker who drew most of the diagrams.

Summary

Photographs of more than a thousand particles traversing a 2 cm. lead block inside a Wilson cloud chamber, were taken at sea level (Bombay). Coulomb and nuclear scatterings of particles capable of going through 5, 15, 25 and 35 cm. of lead were studied. The experimental scattering distributions have been compared, and found to be in fairly good agreement with the theoretical distributions calculated by assuming Williams' scattering distributions, and Wilson's energy spectrum measurements at London. A lower limit of the order of 2 to 3×10^{-28} cm.^{2} per nucleon, for

the nuclear scattering cross-section of mesons has been indicated. This value is in fairly good agreement with the values obtained by most of the experimental workers. The number of large angle scatterings observed is not sufficiently large to study the variation of the nuclear scattering cross-section with energy.

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